CORRELATION OF STRUCTURE AND LUMINESCENCE OF CUPROUS IODIDE PHOSPHINE COMPLEXES OF TYPES: $Cu_4X_4(PR_3)_4$, $Cu_2X_2(PR_3)_3$ AND $CuX(PR_3)_2$

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AND $CuX(PR_3)_2$

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CHAPTER I

INTRODUCTION AND HISTORICAL

Copper(I) halides and a variety of Lewis bases (i.e. N, S and P) form complexes with a wide variety of stoichiometries, structures and emission characteristics in the solid state. There are several kinds of motifs; including rhombs, chairs and cubes common for such copper(I) halide complexes. These complexes may exhibit different emission properties.[1] Cu:X:L stoichiometries of 1:1:1, 1:1:1.5, 1:1:2 have been observed. Common motifs are illustrated in Figure 1.

Many of these complexes will emit in the visible range when excited by ultraviolet light. There are five possible mechanisms of excitation proposed to explain emission behavior in metal ligand complexes.

1) Metal to Ligand Charge Transfer (MLCT)

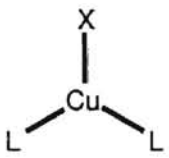
2) Ligand - Ligand Interaction (LLI)

3) Single Metal Excitation (SME)

4) Metal - Metal Interaction (MMI)

5) Donor-Acceptor Pairs (DAP)

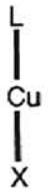
1) Metal to Ligand Charge Transfer (MLCT) ---- an electron from the $3d^{10}$ orbital of copper(I) is excited to a π^* orbital of the aromatic ligand giving $3d^9\pi^*$ as the excited configuration. This transition exists in many copper(I) halide



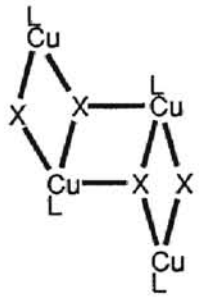
L_2CuX

L_2CuX

$L_{1.5}CuX$



LCuX



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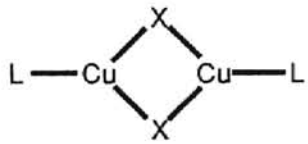

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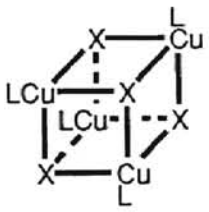

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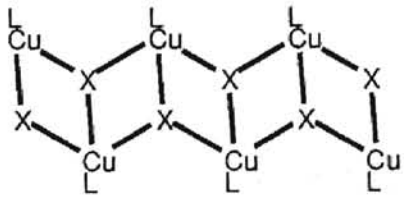

LCuX

L = PR (R = alkyl, aryl)
X = I, Br, Cl

Figure 1. Motifs of Copper(I) Halide Complexes

complexes in which the donor atom is part of an unsaturated system, such as in pyridine or acetonitrile.

2) Ligand-Ligand Interaction (LLI) ---- this is a π-π^* transition between neighboring p systems. It is necessary for the p systems to be packed in parallel fashion and close to each other so that interaction between π and π^* is possible. Emission arises totally from electronic excited states of the ligand system.

3) Single Metal Excitation (SME) ---- this refers to excitation involving a single metal described as a $3d^{10}$ -> $3d^9 4s^1$ transition. The existence of SME in copper(I) complexes may be illustrated by the monomeric CuI complexes of piperidine and morpholine. Both ligands are non-aromatic, therefore neither MLCT and LLI can take place.

4) Metal-Metal Interaction (MMI) ---- this mechanism was proposed for solid copper(I) halide complexes when the copper-copper atoms are less than 2.6Å apart. It is the $3d^{10}3d^{10}$-$3d^9 3d^{10} 4s^1$ excitation and has been supported by molecular orbital calculations. As copper atoms are brought closer together, and only the 3d orbitals are considered, the binding energy becomes more positive while the overlap population becomes negative, indicating repulsion. If 4s and 4p orbitals are considered, the reverse occurs, indicating attractive forces between two near copper atoms.

5) Donor Acceptor Pair (DAP) ---- this mechanism occurs when a ligand donates an electron to the metal atom. *Ab initio* calculations have shown for the system, Cu_2I_2(Lewis base)$_4$, that the HOMO orbital is dominated by iodine p orbitals whereas the LUMO orbitals are dominated by copper based p orbitals. Thus the excitation mechanism involves promotion of an electron from iodine to copper.

In 1938, J. T. Randall published the first account of luminescence of cuprous halides with low frequency ultraviolet radiation.[2,3] He observed a visible

color change of the emission between room temperature and 77 K. Hardt et al[4-9] continued Randall's research and published numerous papers in this field in the early 1970's. Complexes of copper(I) halides with Lewis bases such as pyridine and its derivatives, morpholine, piperidine, quinoline, pyrrolidine, etc. were synthesized and their emission colors recorded. These workers observed that some copper(I) complexes apparently had temperature dependent emission which was called "fluorescence thermochromism." Two phenomena were believed responsible for the change in color of emission with temperature: (a) an actual shift of the λ_{max} or (b) an intensity change of λ_{max} with temperature.

Weber and Hardt[10] attempted to explain the temperature dependent emission observed for copper(I) complexes. They studied the shift of λ_{max} by comparing the powder diffraction patterns of several copper(I) carboxylates which included acetate, formate, propionate and butyrate salts. Thermochromic differences were thought to originate from packing differences because all of the carboxylate structures were of the same general motif. They concluded that those carboxylates with odd numbers of carbon atoms pack more loosely than those with even numbers of carbon atoms. It was postulated that thermochromic emission arose from tight packing while loose packing leads to non-thermochromic emission. They reasoned that loosely packed molecules are more likely to oscillate and to dissipate excited state energy non-radiatively.

Hardt et al[11] observed that thermochromicity of the copper(I) iodide hexamethylenetetraamine (HMTA) complex varies with solvent and with the method of preparation. The fluorescent behavior of this compound varied with temperature. When additional HMTA was added to tighten the structure, the complex became non-thermochromic. The "framework hypothesis" was suggested. If each copper atom in a complex has at least 1.33 ligands available,

then the complex will not display thermochromism, due to the limited mobility in the lattice.

Hardt and Pierre[12], and Schramm and co-workers[13,14] suggested that thermochromicity was related to crystallographic symmetry. They compared emission and crystal structures of [CuI(piperidine)]$_4$, [CuI(morpholine]$_4$ and [CuI(pyridine)]$_4$. Thermochromism is not observed in [CuI(piperidine)]$_4$ which has a 4-fold inversion axis within the cubic cluster, while the other two crystal structures have a twofold axis and no symmetry element respectively. They proposed that if the point symmetry of a (CuI)$_4$ cluster is at least four-fold, then luminescence thermochromism will not be observed.

Rath et al[15,16] pursued investigation of the influence of four-fold symmetry on thermochromicity in two complexes: (CuI)$_4$(paratoluidine)$_2$-(acetonitrile)$_2$ and (CuI)$_4$(parachloroaniline)$_2$-(acetonitrile)$_2$. The possibility of an internal four-fold symmetry element was removed because of the mixed ligands. Both complexes emitted non-thermochromically and displayed no shift of emission maxima. For these two tetrameric complexes, the average Cu···Cu distances are 2.699(3) and 2.682(7) Å respectively and the two emission maxima, 586 nm and 630 nm, were thought most likely due to metal centered interactions.

Tompkins et al[17], continued the investigation of the influence of symmetry on the emission of a compound. Complexes with cubic motifs and different symmetry elements were prepared. (CuI(isopropylnicotinate))$_4$ crystallizes with a four bar symmetry element in the center of the tetramer; (CuI(phenyl-nicotinate))$_4$ has a two-fold axis relating one-half of the cube to the other; and (CuI(benzylnicotinamide)$_4$ has no symmetry element in the cube. Each complex emitted at a different wavelength and each had a different crystallographic symmetry element, establishing that the presence or absence of symmetry may be correlated with thermochromicity.

Bao et al[18] proposed that crystallographic symmetry may influence the wavelength of maximum emission rather than affecting thermochromicity. The emission of copper(I) complexes due to nonligand based mechanisms was studied (i.e. aliphatic amine complexes). They concluded that in these systems, without ligand centered excited states, emission can only orginate from metal centered electron transitions. Four rhombohedral systems with the $Cu_2I_2L_4$ structure were studied: Cu_2I_2(1-methylpiperazine)$_4$ (I), Cu_2I_2(4-methylpiperidine)$_4$ (II), Cu_2I_2(3,3-dimethylpiperidine)$_4$ (III), and Cu_2I_2(3-azaspiro[5.5]undecane)$_4$ (IV). Complex (III) and (IV) both crystallize with a crystallographic center of symmetry and emit at 650 nm when excited at 330 nm. Structures (I) and (II) have no symmetry element and emit at 495-500 nm under identical conditions. *Ab initio* caculations suggest that the emission is derived from a halide base LUMO to copper based HOMO transition in complexes (I) and (II) which is forbidden by selection rules for complexes (III) and (IV) respectively. These complexes must then display emission by transitions between copper dominated orbitals higher in energy than the LUMO end, which are closer in energy.

Bao's research continued with cubic clusters, $(CuI)_4$(acetonitrile)$_2$(morpholine)$_2$ (V) and (CuI(morpholine))$_4$ (VI). Structure (V) has no symmetry element within the cube, yet emits at 575 nm where as (VI) has a two-fold rotation axis and emits at 640-680 nm. It was concluded that in (VI), the HOMO level was raised by the twofold axis, reducing the energy difference between the HOMO and LUMO levels. Therefore, emission appears at a longer wavelength.

Hu et al[19] studied six ligand-based complex systems of the type, $Cu_4I_4(CH_3CN)_2$(ligand)$_2$ [ligand = (i) 2,6-dimethylaniline, (ii) o-ethylaniline, (iii) o-toluidine, (iv) p-anisidine, (v) p-toluidine and (vi) 6-ethyl-o-touilidine], with either

twofold symmetry or no symmetry, to determine if a correlation between the symmetry element and maximum emission exists. *Ab initio* calculations showed that room temperature emission was only partially correlated with symmetry elements.

Hu et al[20] later studied anionic linear Cu(I) complexes and their emission. Twenty-six complexes of the type, $[CuX_2]^-$, were synthesized and characterized by X-ray diffraction. These complexes were found to have one of the following symmetry operations: center of symmetry, 2-fold axis or no internal symmetry. The compounds emitted at approximately the same wavelengths (465-515nm) and the influence of the halogen atom on emission was negligible. Quenching was observed in solids which crystallized with quaternary aromatic phosphorus atoms as counter ions. *Ab initio* calculations showed that emission of the complexes occurred by a donor-acceptor pair mechanism.

There is no published data linking emission and structural characteristics of copper(I) halides complexed with phosphines. These complexes are of interest because they provide opportunities for control of symmetry element presence. However, numerous crystallographic studies of $CuX(PR_3)$ complexes of rhombohedral, cube and chair form existed in the literature (Tables I-VI). They were expected to display increased stability compared to those complexes with nitrogen ligands. This emission may have potential application in the photosensitization of semiconductors. The focus of the thesis was to prepare cubic complexes of the general type, $Cu_4I_4L_4$, in which the ligands would be substituted phosphine groups. Syntheses were carried out in a variety of solvents and the stoichiometries of the copper(I) halide and ligand were varied in an attempt to prepare as many complexes of this type as possible. A number of complexes whose structures were known in the literature were prepared and identified by determination of cell dimensions, to provide additional emission

data. Crystals were examined by single crystal X-ray analysis. The emission spectra of cubic and rhombic clusters were measured and a correlation of the symmetry of the single crystal motif with the wavelength of maximum emission was sought. This knowledge was sought to gain a better understanding of the correlation of solid state structure with luminescent behavior of solid state complexes.

Table I

Known $[M_4X_4L_4]$ Pseudo-cube core parameters*

Compound	Symmetry	Distances (Å)				Angles(°)			Ref.
		M-X	M-L	M··M	X···X	M-X-M	X-M-X	L-M-X	
$[CuCl(PPh_3)]_4$	2	2.363(2) -2.505(2)	2.192(2) -2.193(2)	3.118(1) -3.430(2)	3.060(3) -3.722(3)	79.71(6) -90.19(6)	88.94(6) -101.11(7)	112.73(7) -131.06(8)	21
$[CuBr(PPh_3)]_4$	2	2.491(2) -2.617(2)	2.206(3) -2.209(3)	3.087(2) -3.541(2)	3.617(2) -4.004(2)	74.96(5) -87.85(5)	90.24(6) -105.55(6)	111.73(8) -127.27(9)	22
$[CuI(PPh_3)]_4$	1	2.653(3) -2.732(2)	2.251(6) -2.258(7)	2.874(5) -3.164(4)	4.234(2) -4.496(3)	67.78(9) -71.75(9)	103.0(1) -115.0(1)	106.5(1) -116.9(2)	23
$[CuCl(PEt_3)]_4$	3	2.438(1)	2.176(2)	3.211(2)	3.657(2)	82.36(5)	97.15(4)	120.02(3)	24
$[CuBr(PEt_3)]_4$	3	2.544(1)	2.199(4)	3.184(2)	3.932(1)	77.48(4)	101.25(3)	116.80(2)	24
$[CuI(PEt_3)]_4$	3	2.684(1)	2.254(3)	2.927(2)	4.380(1)	66.10(4)	109.38(4)	109.56(8)	24
$[CuBr(P(t\text{-}Bu)_3)]_4$	3	2.571(1) -2.604(1)	2.228(3)	3.479(2) -3.491(2)	3.827(1) -3.838(1)	83.95(5) -84.85(5)	94.70(5) -95.74(5)	120.84(8) -122.43(8)	25
$[CuI(PMePh_2)]_4$	2	2.611(1) -2.759(1)	2.250(2) -2.250(2)	2.840(1) -3.010(1)	4.297(1) -4.488(3)	63.37(3) -67.27(4)	107.03(4) -113.39(3)	101.62(6) -121.77(6)	26

* -- ranges are given where appropriate

Table II

Known $[M_4X_4L_4]$ "Step" core parameters*

Compound	Distances (Å) M-X	Distances (Å) M-L	Angles(°) M-X-M	Angles(°) X-M-X	Angles(°) L-M-X	Ref.
$[CuBr(PPh_3)]_4 \cdot 2CHCl_3$	2.4773(21) -2.3765(19)	2.1943(26) -2.2070(33)	71.74(6) -107.15(7)	96.76(6) -110.81(8)	114.86(10) -128.75(11)	21
$[CuI(PPh_3)]_4$	2.5273(22) -2.7281(23)	2.2277(47) -2.2418(39)	64.34(7) -108.29(7)	102.45(7) -117.85(9)	112.00(12) -127.49(14)	24
$[CuBr(PPh_3)]_4$	2.371(3) -2.676(3)	2.206(5) -2.207(4)	68.8(1) -73.8(1)	96.7(1) -112.9(1)	112.2(1) -127.7(1)	23

* -- ranges are given where appropriate

Table III

Known $[M_2X_2L_2]$ Rhombohedral [1:1:1] core parameters*

Compound	Distances (Å) M-X	M-L	M···M	Angles(°) X···X	M-X-M	X-M-X	L-M-X	Ref.
$[CuCl(P(cyclohexane)_3)]_2$	2.285(2) -2.322(2)	2.183(2)	3.066(1)	3.439(3)	83.44(7)	96.56(7)	127.40(7) -136.05(7)	27
$[CuI(P(cyclohexane)_3)]_2$	2.562(1) -2.579(1)	2.225(1)	2.892(1)	4.25	68.48(3)	111.52(3)	123.34(5) -124.93(5)	28
$[CuCl(P(o\text{-}tolyl)_3)]_2$	2.281(3)	2.183(3)	3.130(2)	3.403(3)	85.2(1)	94.8(1)	131.2(1)	29
$[CuBr(P(o\text{-}tolyl)_3)]_2$	2.416(1)	2.198(2)	3.111(1)	3.712(2)	79.94(5)	100.06(4)	129.92(8)	29
$[CuCl(PPh_2Mes)]_2$	2.287(2) -2.329(3)	2.196(2)	3.076(2)	3.447(2)	83.56(8) -135.40(8)	96.44(8)	128.15(7)	30
$[CuBr(PPh_2Mes)]_2$	2.397(2) -2.441(2)	2.198(3)	3.083(2)	3.748(2)	79.18(6) -132.2(1)	100.8(1)	127.0(1)	30
$[CuI(PPh_2Mes)]_2 \cdot 4/3C_6H_6$	2.544(3) -2.584(2)	2.222(5) -2.226(5)	2.690(3)	4.316(2)	62.94(7) -63.71(7)	114.9(1) 114.6(1)	118.3(1) -127.0(1)	30
$[CuCl(PPhMes_2)]_2 \cdot 2MeCN$	2.281(2) -2.326(1)	2.202(2)	3.086(1)	3.422(2)	84.08(5)	95.9(1)	128.0(1) -135.8(5)	30
$[CuBr(PPhMes_2)]_2 \cdot 3C_6H_6$	2.393(2) -2.415(2)	2.197(3)	3.052(3)	3.684(2)	78.80(7)	100.1(1)	128.7(1) -130.9(1)	30
$[CuI(PPhMes_2)]_2 \cdot 2MeCN$	2.552(4) -2.597(3)	2.201(4) -2.264(5)	2.728(3)	4.361(3)	63.49(7) -64.60(6)	115.8(1) -116.0(1)	114.9(1) -128.3(1)	30

* -- ranges are given where appropriate

Table IV

Known $[M_2X_2L_3]$ Rhombohedral [1:1:1.5] core parameters*

Compound	Distances (Å)				Angles(°)			Ref.
	M-X	M-L	M···M	X···X	M-X-M	X-M-X	L-M-X	
$Cu_2Cl_2(PPh_3)_3$	2.247(4) 2.454(4)	2.183(4) -2.245(5)	2.909(2)	3.656(5)	76.1(2) 76.3(2)	97.3(2) 107.1(2)	102.4(3) -133.5(2)	31
$Cu_2Br_2(PPh_3)_3$	2.364(2) -2.571(2)	2.191(2) -2.249(3)	2.898(2)	3.947(2)	71.46(4) 71.79(5)	100.84(5) 111.54(6)	101.20(8) -129.56(9)	23
$Cu_2I_2(PPh_3)_3$	2.500(2) 2.819(1)	2.219(3) -2.267(3)	3.041(3)	4.302(1)	69.43(5) 70.43(4)	102.24(5) 116.37(6)	99.94(8) 130.75(9)	32
$Cu_2Cl_2(PPh_3)_3 \cdot Bz$	2.260(2) 2.292(2)	2.183(3) -2.265(2)	3.138(3)	3.528(3)	82.71(8) 83.01(8)	91.57(8) 101.63(8)	102.96(8) -116.87(9)	33
$Cu_2Br_2(PPh_3)_3$ •1.5 Bz	2.370(2) -2.610(2)	2.190(3) -2.260(3)	2.992(2)	4.009(2)	71.66(5) 71.88(5)	101.44(5) 114.26(1)	102.27(8) -127.03(9)	34
$Cu_2Cl_2(P(CH_3)Ph_2)_3$ •benzene	2.260(2) -2.292(2)	2.21833) 2.265(2)	3.138(3)	3.528(3)	82.71(8) 83.01(8)	91.57(8) 101.63(9)	102.96(8) -134.74(8)	33
$Cu_2I_2(P(m\text{-tolyl})_3)_3$	2.543(1) -2.555(1)	2.236(1) -2.283(1)	3.005(1)		68.6(1) 68.8(1)	104.4(1) 118.0(1)	100.4(1) -109.4(1)	35

* -- ranges are given where appropriate

Table V

Known $[M_2X_2L_4]$ Rhombohedral [1:1:2] core parameters*

Compound	Distances (Å) M-X	M-L	M···M	Angles(°) X···X	M-X-M	X-M-X	L-M-X	Ref.
$[CuBr(PMePh_2)_2]_2$	2.474(1) -2.613(1)	2.258(1) -2.263(2)	2.972	4.120	71.5(1)	108.5(1)	98.7(1) -116.7(1)	36
$[CuI(P(C{=}CC_6H_5)_3)_2]_2$	2.611(1) -2.646(1)	2.255(3) 2.263(3)	2.747(2) -2.872(3)	4.416(1) -4.467(1)	63.2(2) -66.1(2)	113.9(2) -116.8(2)	103.1(2) -110.3(2)	37

* -- ranges are given where appropriate

Table VI

Known core parameters* of [1:1:2] monomeric complexes [MXL_2]

Compound	Distances (Å) M-L	M-X	Angles(°) L-M-L	L-M-X	Ref.
$CuCl(PPh_2\text{-}o\text{-}tol)_2$	2.241(2) -2.257(2)	2.205(2)	126.96(7)	113.61(7) -118.55(7)	38
$CuBr(PPh_2\text{-}o\text{-}tol)_2$	2.240(2) -2.255(2)	2.336(1)	127.89(7)	112.52(6) -118.25(6)	38
$CuI(PPh_2\text{-}o\text{-}tol)_2$	2.255(1)	2.507(1)	126.36(7)	116.82(4)	38
$CuCl(PPh_3)_2 \cdot 0.5$ Bz	2.260(2) -2.272(2)	2.208(2)	125.48(7)	113.76(7) -120.74(6)	38
$CuBr(PPh_3)_2 \cdot 0.5$ Bz	2.263(2) -2.282(3)	2.346(2)	126.0(1)	112.8(1) -121.0(1)	39
$CuI(PPh_3)_2$	2.273(2)	2.524(2)	126.9(1)	116.61(5)	38
$CuI(P(C_6H_{11})_3)_2$	2.2753(12) -2.2846(12)	2.5913(7)	134.06(4)	110.99(3) -114.79(3)	28

* -- ranges are given where appropriate

CHAPTER II

X - RAY CRYSTALLOGRAPHY

X-ray crystallography is the determination of the three-dimensional structure of molecules in the crystalline state by analysis of X-ray diffraction data. This method of structural elucidation can provide not only composition, connectivity, interatomic distances, bond angles, conformation and chirality, but also knowledge about the areas of electron density occupied by the atoms.

In order for a molecule to diffract, it must be crystalline. A crystal is a substance having a systematic arrangement of atoms, ions or molecules. Every crystal has a lattice as its geometric basis. This arrangement can be represented by a unit or motif called the unit cell. These unit cells are arranged in an ordered fashion to form the crystal whereby each cell is characterized by three edges: a, b and c, and three angles between these edges: α, β and γ. Depending upon the relationships between the cell edges and angles, the crystal will belong to one of seven crystal classes. These classes only define the shape of the volume of the unit cell (Table VII).[40]

Table VII

THE SEVEN CRYSTAL CLASSES

Crystal system	Unit cell shape
Triclinic	$a \neq b \neq c$, $\alpha \neq \beta \neq \gamma \neq 90°$
Monoclinic	$a \neq b \neq c$, $\alpha = \gamma = 90°$, $\beta \neq 90°$
Orthorhombic	$a \neq b \neq c$, $\alpha = \beta = \gamma = 90°$
Tetragonal	$a = b \neq c$, $\alpha = \beta = \gamma = 90°$
Rhombohedral	$a = b = c$, $\alpha = \beta = \gamma \neq 90°$
Hexagonal	$a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$
Cubic	$a = b = c$, $\alpha = \beta = \gamma = 90°$

Within each unit cell there may be symmetry elements relating atoms or molecules to each other. These operations may include any of the following:

1. rotation axes --- must be parallel or coincident to an axis
2. mirrors --- planes of reflection, must be perpendicular to an axis and parallel to one of the crystal faces
3. inversion axes --- combination of a rotation axis with a center of symmetry
4. glide plane --- combination of a mirror plane and a translation
5. screw axes --- combination of a rotation axis and translation parallel to the axis

These elements, together with the seven crystal classes and centering possibilities (body, face or primitive), form a set of 230 structural arrangements known as space groups.

Crystalline materials are capable of diffracting radiation which has a wavelength similar in magnitude to the crystal's interatomic separations. Diffraction by a crystal occurs only when Bragg's law is satisfied:

$$n\lambda = 2d\sin\theta \qquad (1)$$

where n is an integer number; λ is the radiation wavelength; θ is the angle of incidence and the angle of diffraction of the X-ray beam, d is the perpendicular

distance, in angstroms, between the two lattice planes. When Bragg's law is satisfied, the diffracted beams are in phase and positively enforce each other.

The diffraction data must be corrected for four different experimental artifacts. Correction factors are applied for (i) background, (ii) polarization, (iii) Lorentz effect, and (iv) crystal decomposition.[41,42] Correction for left and right-background is calculated using the following equation.

$$I_{int} = (I_{meas} - L_{bg} - R_{bg}) \times \text{Scan speed} \quad (2)$$

where:

I_{int} = Integrated intensity

I_{meas} = Measured intensity

L_{bg} = Left-background

R_{bg} = Right-background

and the error in the intensity measurement is calculated by:

$$\sigma I_{int} = \sqrt{(I_{meas} + L_{bg} - R_{bg})} \times \text{Scan Speed} \quad (3)$$

where:

σI_{int} = Standard deviation of I_{int}

The reflection is considered to be observed if the following condition is met:

$$I_{int} > 3\sigma I_{int} \quad (4)$$

The data must also be corrected for polarization and Lorentz effects such that:

$$\left(\frac{KI_{int}}{Lp}\right) = I_{cor} \quad (5)$$

where K = constant, based on crystal size, beam intensity and machine constants.

L = Lorentz factor

p = Polarization factor

(i) *Polarization factor* ---- The polarization term (p) arises because the fact that efficiency of diffraction of the components of the X-ray beam varies with diffraction angle. If we consider the X-ray beam to contain only the limiting components (1) a component ($I_{||}$) parallel to the diffracting plane, and (2) a perpendicular component ($I_{\perp}$), these limiting components of the incident beam are diffracted with differing efficiencies and the ratio of these differences varies with the 2θ angle. At low 2θ, the $I_{||}$ and $I_{\perp}$ beams are diffracted with near equal efficiency. At high 2θ the efficiency of diffraction of the $I_{\perp}$ component decreases dramatically, causing the diffracted beam to become partially polarized. The polarization factor, P, is a function of 2θ and is independent of the geometry of data collection and is calculated by the following expression.

$$P = \frac{(1 + \cos^2 2\theta)}{2} \qquad (6)$$

(ii) *Lorentz factor* ---- The Lorentz factor (L) is necessary because when the crystal is rotated at a constant speed, reflections with low 2θ spend more time in the beam than reflections with high 2θ. The correction is defined so as to remedy this effect

$$L = \frac{1}{(\sin 2\theta)} \qquad (7)$$

The two factors, Lorentz and polarization, may be combined into a single trigonometric expression called Lorentz-polarization factor (LP) which is given by:

$$LP = \frac{(1 + \cos^2 2\theta)}{2\sin 2\theta} \qquad (8)$$

(iii) *Absorption factor* ---- When the crystal absorbs the diffracted beam, it reduces its intensity. The extent of the absorption depends on the path length of the beam through the crystal, the nature of the atoms in the crystal, and the wavelength of the incident X-ray beam. The absorption factor (A) is defined by the following mathematical expression:

$$A = \left(\frac{1}{V}\right)\int e^{-\mu L} dv \qquad (9)$$

where μ is the linear absorption coefficient, L is the path length through the crystal, V is the volume of the crystal and dV is the change in volume.[43]

(iv) *Decomposition factor* ---- This factor assumes that decomposition of a crystal is linear with respect to time. This leads to a decrease in the intensity as the data collection proceeds. Thus the decomposition correction factor (D) is given by:

$$D = I_{orig}/I_{ave} \qquad (10)$$

where:

I_{orig} = original intensity of the standard reflection

I_{ave} = average current intensity of the standard reflection

When all four factors are taken into account, they may be combined to form an overall corrected intensity:

$$I_{corr} = I_{int} \times (LP)^{-1} \times A^{-1} \times D \qquad (11)$$

where I_{int} is the integrated intensity and I_{corr} is the corrected intensity.

The structure factor, $|F_{hkl}|$, expressing the combined scattering of all atoms in the cell compared to that of a single electron, is determined as the square root of the corrected integrated intensity, I_{corr}:

$$|F_{hkl}| = K_s \sqrt{I_{corr}} \qquad (12)$$

where K_S is a scale factor. The error in F_{hkl}, σF, is calculated according to the following expression:

$$\sigma F = \frac{1}{2}\sqrt{\frac{k}{Lp}}\frac{\left[N_t + N_{lbg} + (0.01N_{pk})^2\right]}{\sqrt{(N_t - N_{lbg} - N_{rbg})}} \qquad (13)$$

where:

N_t = number of counts

N_{lbg} = number of left background counts

N_{rbg} = number of right-background counts

$$N_{pk} = N_t - N_{rbg} - N_{lbg}$$

To obtain a three dimensional electron density map, amplitudes of the structure factors and their phases must be known. However, the measurement contains no information about the phase (α), because phases cannot be measured.[42,44-46] A phase is defined as the difference in period, expressed as an angle, between the wave resulting from a specific set of planes and a wave resulting from scattering at the origin.

$$\alpha_{hkl} = \tan^{-1} \frac{B_{hkl}}{A_{hkl}} \qquad (14)$$

Consequently, to find the atomic positions in a model, we must determine the phase angles and use a Fourier transformation of αF, generating an interpretable electron density map showing the atomic positional parameters.

The phase problem can be solved by two mathematical approaches: direct methods or the Patterson method. The Patterson method, also known as the "Heavy Atom Method," may be used only for structures which contain a heavy atom greater in weight than sulfur. A Patterson map is the Fourier transform of $|F|^2$, in which the phase angle's sign is eliminated. The Patterson function, P (u,v,w), is defined such that:[44]

$$P(u, v, w) = 1/V_c \sum_h \sum_k \sum_l |F_{hkl}|^2 \cos 2\pi(hu + kv + lw) \qquad (15)$$

or

$$P(u, v, w) = V \iiint \rho(x+u, y+v, z+w)\, dxdydz \qquad (16)$$

This function is always centrosymmetric. It defines a map which gives interatomic distances plotted from the origin. A peak in the Patterson map, called a vector, at (u,v,w) implies that there are two atoms in a crystal structure at (x_1, y_1, z_1) and (x_2, y_2, z_2) such that (x_2-x_1=u, y_2 -y_1=v, z_2-z_1=w). Because the vectors between heavy atoms are the most visible, a map is interpreted only for heavy atom information by the use of the space group general equivalent

positions. These allow for the calculation of Harker planes and lines. From these vectors, positional parameters for the heavy atoms can be determined.

The second tactic most commonly used to obtain positional parameters for the atoms is called direct methods. This tactic is applicable to both light and heavy atom structures. Direct methods is a way of determining the phase(s) based on relationships among the intensities of the reflections themselves. The first step in this solution, requires the conversion of the observed intensities into normalized structure factors by the following equation:

$$|E_{hkl}|^2 = \frac{|F_{hkl}|^2}{\sum f_i^2} \qquad (17)$$

where

$|E_{hkl}|$ = normalized structure factor

When the structure factors are normalized, the effects of the decline in atomic scattering power with increasing 2θ are eliminated.

The phases of a subset may be derived directly from the magnitudes of the $|F_{hkl}|^2$. This value will allow for the calculation of an electron density map providing a means to derive a suitable structure from the interpretation of this map.

Direct methods are based on the premise that the electron density in a real crystal can never be negative and that the electron density consists of discrete spherically symmetric atoms. For a centrosymmetric structure, with each atom at (x, y, z) matched by an equivalent structure (-x, -y, -z), the phase angle can only be either 0° or 180°. Therefore from the following equation:

$$\rho(xyz) = \left(\frac{2}{Vc}\right)\sum_h\sum_k\sum_l |F_{hkl}|\cos\left[2\pi(hx+hy+lz)-\alpha\right] \qquad (18)$$

where:

$\rho(xyz)$ = the electron density at some point (x, y, z) in the cell

Vc = unit cell volume

$|F_{hkl}|$ = amplitudes of structure factors

α = phase angle

can be simplified even further to the following expression:

$$\rho(xyz) = \left(\frac{2}{Vc}\right)\sum_h\sum_k\sum_l \pm|F_{hkl}|\cos 2\pi(hx+hy+lz) \qquad (19)$$

Equation (19) may have two different signs. This equation takes a positive sign when $\alpha = 0°$ and $\alpha = 180°$ for a given structure factor. Thus, the electron density map can be calculated from the following equation when the signs of a significant number of structure factors are known.

$$\rho(xyz) = \left(\frac{2}{Vc}\right)\sum_h\sum_k\sum_l \pm|E_{hkl}|\cos 2\pi(hx+hy+lz) \qquad (20)$$

Phases are allocated through the application of Harker-Kasper inequalities. Harker and Kasper (1936) made use of Couchy's inequality (eqn

$$\left|\sum_{j=1}^{t} a_j b_j\right|^2 \leq \sum_{j=1}^{t}|a_j|\sum_{j=1}^{t}|b_j| \qquad (21)$$

21) to show that inequalities exist between certain structure factors in centrosymmetric crystals. Applying this equation to the centrosymmetric unitary structure factor equation produces the following relationship:

$$U_{\mathbf{h}}^2 \leq \frac{1}{2}(1+U_{2\mathbf{h}}) \qquad (22)$$

where

U = unitary structure factor

The sign of $U_{2\mathbf{h}}$ may be positive or negative. Two further inequalities may be derived by adding and subtracting two unitary structure factors and applying equation (21):

$$(U_{\mathbf{h}}+U_{\mathbf{h}'})^2 \leq (1+U_{\mathbf{h}+\mathbf{h}'})(1+U_{\mathbf{h}-\mathbf{h}'}) \qquad (23)$$

and

$$(U_{\mathbf{h}}-U_{\mathbf{h}'})^2 \leq (1-U_{\mathbf{h}+\mathbf{h}'})(1-U_{\mathbf{h}-\mathbf{h}'}) \qquad (24)$$

These two equations may be combined together to obtain the sign of one of $U_{\mathbf{h}}$, $U_{\mathbf{h}'}$, $U_{\mathbf{h}+\mathbf{h}'}$, when the signs of the other two are known by the following expression:

$$\left(|U_{\mathbf{h}}|-|U_{\mathbf{h}'}|\right)^2 \le \left\{1+s(\mathbf{h})s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}')|U_{\mathbf{h}+\mathbf{h}'}|\right\} \left\{1+s(\mathbf{h})s(\mathbf{h}')s(\mathbf{h}-\mathbf{h}')|U_{\mathbf{h}-\mathbf{h}'}|\right\} \quad (25)$$

to show that either one or both of the following relationships are true:

$$s(\mathbf{h})s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}') = +1 \quad (26)$$

and

$$s(\mathbf{h})s(\mathbf{h}')s(\mathbf{h}-\mathbf{h}') = +1 \quad (27)$$

where s(**h**), s(**h'**) and s(**h+h'**) represent the sign of $U_{\mathbf{h}}$, $U_{\mathbf{h}'}$, and $U_{\mathbf{h}+\mathbf{h}'}$ respectively. Symbollic addition then can be used to expand the number of phases using the triplet relationship known as the Sayre equation: [40,47]

$$s(\mathbf{h}_1,\mathbf{k}_1,\mathbf{l}_1)\bullet s(\mathbf{h}_2,\mathbf{k}_2,\mathbf{l}_2) \approx s(\mathbf{h}_1+\mathbf{h}_2,\mathbf{k}_1+\mathbf{k}_2,\mathbf{l}_1+\mathbf{l}_2) \quad (28)$$

where s is "sign of", the mathmatical symbol "≈" means a statistical probability rather than an exact equation, and (h_1,k_1,l_1), $(h,_2k_2,l)_2$ and $(h_1+h_2,k_1+k_2,l_1+l_2)$ are all strong reflections with high |E| values. Therefore, if two of the signs in the equation are known, the third can be deduced from the equation. After a sufficient number of phases are known, a trial structure can be determined. Missing atoms can be located by the difference Fourier $\left|\left(|F_{obs}|-|F_{calc}|\right)\right|$.

Once all atoms are positioned by either mathematical solution method, phased structure factors (F_{calc}) can be calculated and compared with those that have been measured (F_{obs}). The correctness of the model is indicated by the 'Residual factor', R_f, defined as:

$$R_f = \frac{\left(\sum\left||F_{obs}|-|F_{calc}|\right|\right)}{\left(\sum|F_{obs}|\right)} \quad (29)$$

where:

$$F_{calc} = a + ib$$

$$a = \sum f \cos 2\pi(hx_1 + ky_1 + lz_1)$$
$$b = \sum f \sin 2\pi(hx_1 + ky_1 + lz_1)$$

After this initial R factor is determined, refinement of the positions of atoms in the crystal structure is performed using the least-squares method. The least-squares program fits the observed structure amplitudes to the calculated amplitudes. Then the parameters of the atomic positions are altered so that the least squares fit improves. As the model approaches completion, the difference between F_{obs} and F_{calc} is reflected in a lower R_f value.

Each atom has an associated temperature parameter. This value signifies the effect of spreading the electron cloud over a volume. This factor reflects the decrease in the atomic scattering factors as 2θ increases. It is given by the expression:

$$\exp\left[\frac{-B_{iso}(\sin^2\theta)}{\lambda^2}\right] \qquad (30)$$

where B_{iso} is the isotropic thermal parameter. The atomic scattering behavior may be more accurately expressed by the anisotropic thermal parameter:

$$\exp\ -(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + b_{12}hk + b_{13}hl + b_{23}kl) \qquad (31)$$

where b is the individual anisotropic thermal parameter of the atom.

Hydrogen atom positions are usually calculated using idealized geometry. When all atoms have been located, an appropriate weighting scheme and extinction correction may be selected. The refinement is considered complete when the R factor reaches a value of less than 6%. All atoms must in chemically reasonable positions.

Tables of crystal information, data collection conditions, positional parameters, anisotropic thermal parameters and bond distances and angles are prepared. The table of final F_{obs} and F_{calc} structure factors is also printed. Three dimensional drawings of the molecule and the unit cell are prepared

showing atoms as ellipsoids of 90% probability. From these data, structural characteristics can be interpreted including bond type, atomic hybridization, and electron location.

CHAPTER III

LUMINESCENCE

Luminescence occurs when visible radiation is emitted by molecules or atoms that have been excited by absorption of electromagnetic radiation. The radiation wavelength absorbed and emitted is characteristic of the particular luminescent material. There are several types of luminescence which depend upon how the emitter is excited:[48-51]

bioluminescence ---- subsequent to excitation in biological process,

cathodoluminescence ---- excitation occurs using cathode rays of electrons,

chemiluminescence ---- occurs when a chemical reaction supplies excitement,

electroluminescence ---- uses electrical energy to excite,

photoluminescence ---- uses photons or light (often UV) for excitation,

radioluminescence ---- occurs when radioactive particles interact,

sonolumincescence ---- is caused by excitation by ultrasonic waves,

triboluminescence ---- is caused by mechanical interaction.

Photoluminescence is the major area of interest and will henceforth be simply called luminescence. The first process is absorption leading to two operations: radiative and nonradiative decay. Nonradiative decay is vibrational relaxation whereby energy is lost by converting it to vibrational or thermal energy. Radiative decay is also known as fluorescence which is the immediate

reemission of energy in the form of visible light. Of these two operations, fluorescence is the process of primary interest.

Fluorescence is the emission from an excited singlet state (S_1 or S_2) to the ground state(S_0). Phosphorescence results from decay from a triplet state(T_1) to the ground state. For this process, multiplicities of the states where emission originates and terminates differ (Figure 2).

The lifetime is the time a molecule stays in an excited state before returning spontaneously to a lower state with emission of light. Phosphorescence has a lifetime of 10^{-6} to 100 seconds. Fluorescence has a lifetime of 10^{-6} to 10^{-9} seconds or less. Therefore it is impossible to observe fluorescence after excitation ceases.

To study luminescent properties of materials, a fluorometer is usually used. This instrument measures the light emitted for the sample at right angles to the path of the incident or excitation beam. These machines have three main parts: a radiation source, a sample cell, and a detector. An experimental arrangement for the determination of an emission spectrum is shown schematically in Figure 3.

The radiation source is normally a mercury or xenon arc lamp, both provide bright and powerful sources of ultraviolet radiation. Mercury lamps give very high intensity radiation but have a less continuous spectrum than the xenon arc. Xenon lamps give radiation with lower intensity and produce a small number of lines in the 4000 Å and 6000-8000 Å region. In high resolution work, these could produce errors, but are not a problem in low resolution studies. Sources of radiation must be cooled by water or forced air to avoid overheating.

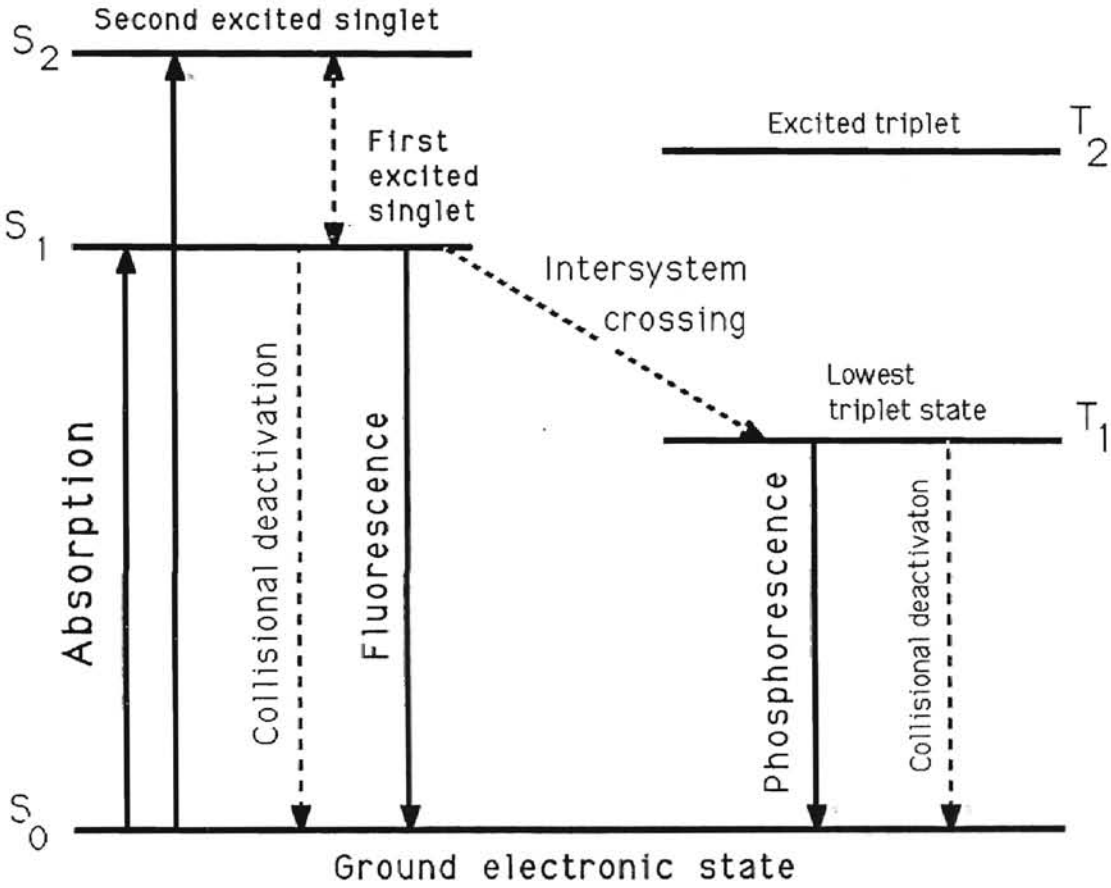

Figure 2. Energy Level Diagram Showing Fluorescence and Phosphorescence Transitions[53]

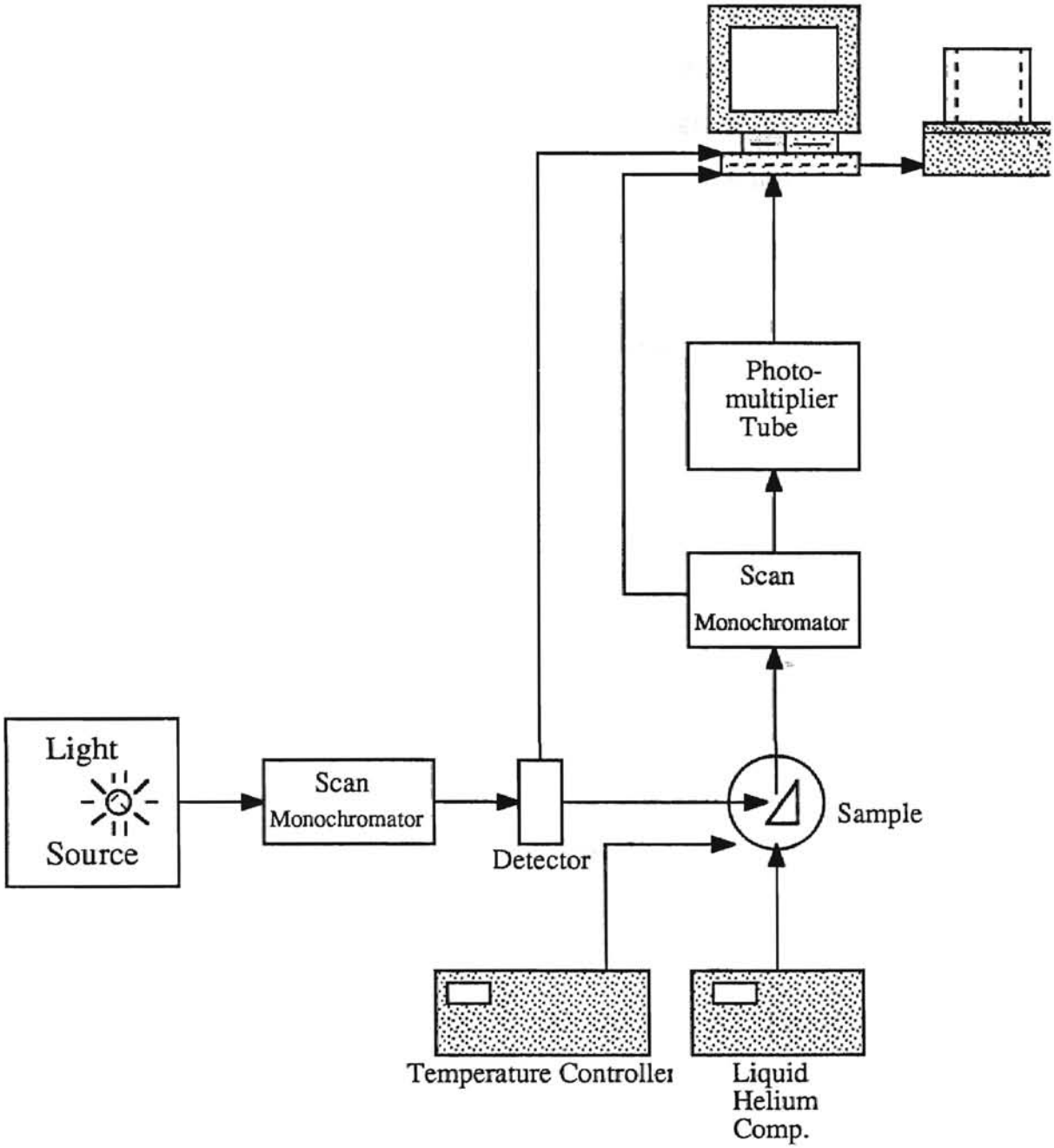

Figure 3. Schematic diagram of a Typical Fluorometer[52]

Monochromators separate light into bands of narrow wavelength by use of gratings or prisms. These are placed before and after the sample chamber to select the excitation and emission wavelengths. Grating monochromators result in a lower loss of intensity and transmit light of shorter wavelength in the visible or red regions, while prism monochromators absorb radiation. Prism materials should have minimal absorbance in the wavelength region of interest. In the UV region, quartz prisms are appropriate. Calibration of the monochromators is done using known emission lines from a mercury lamp.

The sample cell is placed at 90° to the incident beam and emission detector in the sample chamber. The cell's windows must not emit and must be transparent to wavelengths of interest. Usually these sample chamber windows are made of pyrex glass or fused synthetic silica and quartz.

Detectors are often high gain photomultiplier tubes with high voltage power supplies or semiconductor photodiodes. The material of the photocathode can affect the wavelength response, so one with maximum response in the spectral region of interest is necessary. Photomultiplier tubes require correction because of their response to different wavelengths. The output is recorded on magnetic media, floppy disk or tape, and can also be displayed by strip recorder. After correction for irregularities in source lamp intensity, monochromator response, and background effects, the data can be plotted as intensity against wavelength.

CHAPTER IV

EXPERIMENTAL

Materials. All chemicals were reagent-grade materials used without further purification.

[CuBr(PMePh$_2$)]$_4$:

Methyldiphenylphosphine (1.5g, 7.5 mmol) was injected into a slurry of CuBr (2.0g, 139 mmol) in toluene (50 mL) under positive nitrogen pressure. The reaction mixture was heated to 80-90°C, with constant stirring for 24 hours. Gravity filtration was used to remove any excess CuBr present in the mixture. The filtrate was cooled gradually and clear, colorless spheric crystals appeared after several days. They were then collected and recrystallized. A crystal with appropriate dimensions was glued on a glass fiber for X-ray structural analysis.

[CuI(Me$_2$Ph)]$_4$:

Approximately 0.8 mL of PMePh$_2$ (1.5g, 7.5 mmol) was injected into a slurry of CuI (2.0g, 105 mmol) in 2-methoxyethanol (35 mL) under positive nitrogen pressure. The reaction mixture was heated to 80-90°C, with constant stirring for 6 hours. Gravity filtration was used to remove any excess CuI present in the mixture. The filtrate was cooled gradually and clear, colorless plates appeared after several days. They were then collected and recrystallized from toluene. A crystal with appropriate dimensions was mounted on a glass fiber for structural determination using X-ray diffraction.

[CuIP(*m*-toly)$_3$]$_4$:

CuI (0.50 g, 26 mmol) was dissolved in a 25 mL mixture of toluene/acetonitrile (50/50) and 0.20 g (65 mmol) of tri-*m*-tolylphosphine was added to the solution. The mixture was heated to boiling until all solid went into solution. The solution was allowed to stand at room temperature under normal atmospheric conditions. Small colorless cubic crystals formed on slow evaporation of the solvent. A suitable crystal of appropriate size was mounted on a glass nib for use in X-ray structural analysis.

[CuIP(*p*-toly)$_3$]$_4$:

CuI (0.50 g, 26 mmol) was dissolved in 25 mL of toluene and 0.20 g (65 mmol) of tri-*p*-tolylphosphine was added to the solution. The mixture was heated to boiling until all solid went into solution. The solution was allowed to stand at room temperature under normal atmospheric conditions. Small colorless cubic crystals formed on slow evaporation of the solvent. A suitable crystal of appropriate size was mounted on a glass nib for use in X-ray structural analysis.

[CuBrP(*p*-toly)$_3$]$_4$:

CuBr (0.50 g, 28 mmol) was dissolved in 25 mL of toluene and 0.20 g (65 mmol) of tri-*p*-tolylphosphine was added to the solution. The mixture was heated to boiling until all solid went into solution. The solution was allowed to stand at room temperature under normal atmospheric conditions. Small colorless cubic crystals formed on slow evaporation of the solvent. A suitable crystal was mounted on a glass nib for use in X-ray structural analysis.

[CuI(P(*o*-toly)$_3$)]$_2$ • [C_6H_5Me]:

A mixture of 0.5g (26 mmol) cuprous iodide, 0.2g (65 mmol) tri-*o*-tolylphosphine and 25.5 ml of toluene was heated to boiling, filtered and allowed to cool to room temperature under normal atmospheric conditions. After slow evaporation of the solvent, small colorless cubic crystals formed that didn't fluoresce under U.V. light source. A crystal with appropriate dimensions was glued on a glass fiber for X-ray structural analysis.

[$Cu_2Br_2(P(m\text{-tol})_3)_3$]:

CuBr (0.25g, 17 mmol) was injected into a slurry of tri-*m*-tolylphosphine (0.2g, 6 mmol) in benzene (25 mL) under atmospheric conditions. The reaction mixture was heated to boiling, with constant stirring for 2.5 hours. The solution was filtered and allowed to stand at room temperature. Small colorless elongated rhombic clusters formed on slow evaporation of the solvent. A crystal with appropriate dimensions was mounted on a glass fiber for structural determination using X-ray diffraction.

[$CuBr(P(C_6H_{11})_3)_2$] (hexane):

Tricyclohexylphosphine (0.2g, 47 mmol) was injected into a slurry of CuBr (2.0g, 139 mmol) in hexane (35 mL) under positive pressure of nitrogen. The reaction mixture was heated to boiling, with constant stirring for 4 hours. The solution was filtered and allowed to stand at room temperature under normal atmospheric conditions. Small colorless elongated cubic clusters formed on slow evaporation of the solvent that didn't fluoresce under U.V. light source. A suitable crystal was mounted on a glass nib for use in X-ray structural analysis.

[$CuBr(P(C_6H_{11})_3)_2$] (benzene):

Tricyclohexylphosphine (0.4g, 94 mmol) was injected into a slurry of CuBr (1.0g, 64 mmol) in benzene (15 mL) under atmospheric conditions. The reaction mixture was heated to boiling, with constant stirring for 4 hours. The solution was filtered and allowed tc stand at room temperature. Small colorless elongated rhombic clusters formed on slow evaporation of the solvent that fluoresce under U.V. light source. A crystal with appropriate dimensions was glued on a glass fiber for X-ray structural analysis.

$[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$:

Copper(I) iodide (0.50 g, 26 mmol) was dissolved in 35 mL of toluene and 0.32 g (11 mmol) of diphenyl-*p*-tolylphosphine was added to the solution. The reaction mixture was heated to 60-70°C, with constant stirring for 4 hours. Gravity filtration was used to remove any excess CuI present in the reaction mixture. The filtrate was cooled gradually and clear, colorless plates appeared after several days. A suitable crystal of appropriate size was mounted on a glass nib for use in X-ray structural analysis.

$Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$:

ZnI (0.50 g, 2.6 mmol) was dissolved in 50 mL of pyridine and 0.25 g (13 mmol) of CuI was added to the solution. The mixture was heated to boiing until all solid went into solution. It was then allowed to stand at room temperature under normal atmospheric conditions. Large purple rhombohedral crystals formed on slow evaporation of the solvent. A crystal with appropriate dimensions was fixed in a glass capillary filled with nujol to prevent decompostion and mounted on a goniometer for X-ray structural analysis.

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Crystals with appropriate dimensions ($\leq$0.2 mm in all three dimensions) of each compound were chosen for X-ray diffraction. A single crystal of good quality was attached to a glass fiber held in a brass support (Figure 4). The brass pin was placed in a goniometer head and mounted on a Siemens P4 automated four-circle diffractometer equipped with a PC-486DX computer (Figure 5). The samples were irradiated with molybdenum radiation at an average wavelength of 0.71073 Å ($k_{\alpha 1}$ and $k_{\alpha 2}$). Unit cell dimensions were determined using the centered angles for up to 100 strong reflections which were refined with

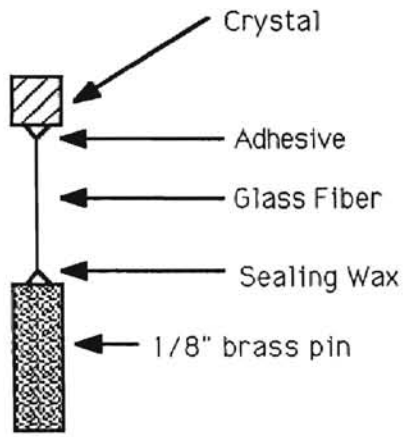


Figure 4. Mounted Crystal

least-squares methods by the automated procedure in XSCANS.[54] The intensity data were collected at room temperature using a variable scan rate, a θ-2θ scan mode and a scan range of 0.6° below $k_{\alpha 1}$ and 0.6° above $k_{\alpha 2}$ to a maximum 2θ value (normally 50.0° and limited by the observed diffraction of the crystal). Backgrounds were measured at the ends of the scan range for a combined time equal to the total scan time. The intensities of three standard reflections were

remeasured after every 97 reflections. The raw intensity data collected were corrected for Lorentz, polarization, absorption, decomposition, centering and background effects, after which redundant and space group forbidden data were removed ($F = \sqrt{I_{corr}}$).

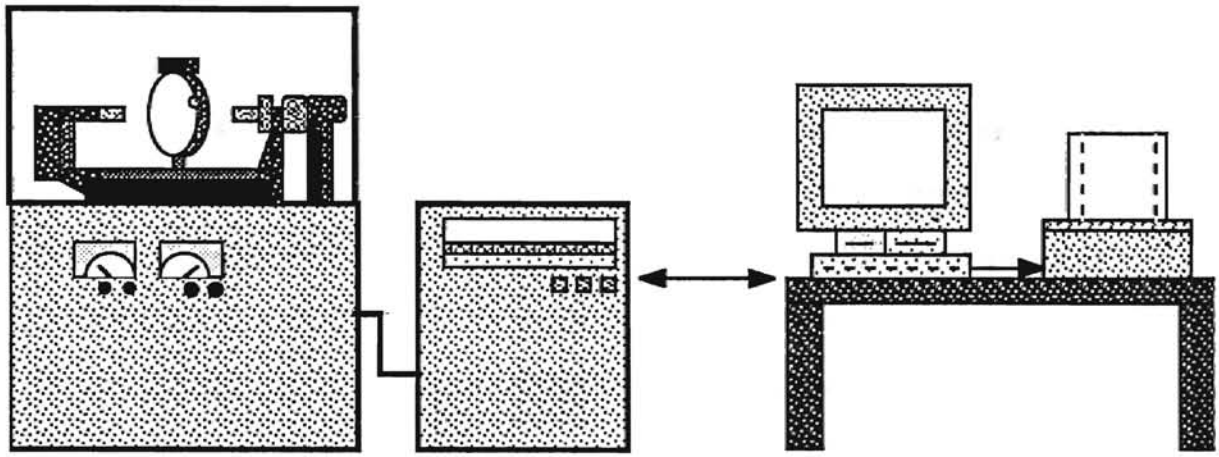


Figure 5. Siemens P4 automated 4-circle diffractometer with PC-486DX computer and printer

Observed reflections (F>4.0 σF) were used to search for the non-hydrogen atom positions by direct or Patterson methods.[55-57] Refinement of the scale factor, positional and anisotropic thermal parameters for all atoms was carried out by either XLS(refinement on F) or SHELXL[58] (refinement on F^2) to convergence. Scattering factors were taken from the International Tables for Crystallography. Hydrogen atom positions were calculated by using idealized geometry. The profile fitting technique for data reduction was employed when necessary. Furthermore, an empirical absorption correction was applied in the final stages to remove inequalities due to differing lengths of pathways through the crystal. A weighting scheme $\left(w = \frac{1}{\sigma^2(F) + |g|F^2} \right)$ and extinction correction were applied at the last stages of refinement. Final refinement led to the agreement factor, R.

FLUORESCENCE

The fluorescence emission spectra of all compounds were measured using an Oriel modular spectrofluorometer equipped with an Apple IIc computer. The sample was prepared as a finely ground powder spread on double-sided tape. The powder was then affixed to a 0.5 X 1.5 inch piece of non-emitting paper. A Xe lamp was used as the light source. Measurements were made from 350-700 nm at 0.2 nm intervals with a scan speed of 1 nm/sec at temperatures 10K and 295K (low temperature measurements were accomplished with the aid of a CTI cryogenic cooler).

The emission spectrum was obtained by irradiating the sample at 300 nm and observing the emitted fluorescence with a scanning monochromator. This provided a plot of intensity versus wavelength. Data were corrected for inhomogeneities of monochromator performance and window transmission before plotting. In addition, intensity scales are reported in arbitrary units due to lack of standardization of sample preparation.

CHAPTER V

RESULTS AND DISCUSSION

During the course of this research, eleven new complexes of copper(I) halides with phosphine ligands were synthesized and structurally characterized by X-ray diffraction. Five were cubes of the formula Cu_4X_4; $Cu_4Br_4(PMePh_2)_4$, $Cu_4I_4(PMe_2Ph)_4$, $Cu_4I_4(P(p\text{-toly})_3)_4$, $Cu_4Br_4(P(p\text{-toly})_3)_4$, and $Cu_4I_4(P(m\text{-toly})_3)_4$; two rhombohedra of formula Cu_2X_2: $Cu_2I_2(P(o\text{-toly})_3)_2\cdot(C_6H_7)$ and $Cu_2Br_2(P(MePh_2))_3$; two forms of the monomeric [1:1:2] complex, $CuBr(P(C_6H_{11})_3)_2$ and two additional complexes: $[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$ and $[Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)]_4\cdot 2C_5H_5N$. The emission from each complex was measured at two temperatures, 10K and 298K, with an excitation wavelength of 300 nm. A summary of the emission data including that from complexes reprepared from the literature, along with their space groups and internal symmetry elements can be found in Table IX.

A tabulation of Cu-X, Cu-P, Cu···Cu' and X···X' distances, X-Cu-X', Cu-X-Cu' and P-Cu-X angles for phosphine complexes prepared in this research is shown in Table X. Data for the additional phosphine complexes from the literature is included for comparison (Tables I - VI). Complete crystallographic data and results for all complexes prepared in this study are presented in Tables XI - LXI.

A. Cubic clusters

The main class of compounds studied were cubes of the type $[Cu_4X_4L_4]$, where the symbol L represents a trialkyl phosphine ligand. Three cubic clusters,

$[CuIP(C_6H_5Me\text{-}p)_3]_4$ (distances averaged: Cu-I, 2.690(3)Å; Cu-P, 2.246(8)Å; I-Cu-I', 106.63(3)°; Cu-I-Cu', 71.01(3)°); $[CuBrP(C_6H_5Me\text{-}p)_3]_4$ (avg. distances: Cu-Br, 2.557(3)Å; Cu-P, 2.22(7)Å; Br-Cu-Br', 100.1(1)°; Cu-Br-Cu', 79.2(1)°) and $[CuIP(C_6H_5Me\text{-}m)_3]_4$ (avg. distances: Cu-I, 2.718(8) Å; Cu-P, 2.217(20) Å; I-Cu-I', 96.86(3) °; Cu-I-Cu', 78.02(3)°) crystallized in various crystallographic space groups but all possess an internal three fold axis. This three-fold axis passes diagonally through the cube with one copper and one halide atom on the axis.

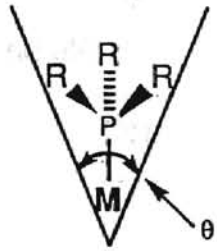
Two additional cubic clusters were prepared with an internal two-fold axis: $[CuI(PMe_2Ph)]_4$ (distances averaged: Cu-I, 2.704(3)Å; Cu-P, 2.246(7)Å; I-Cu-I', 111.7(1)°; Cu-I-Cu', 64.0(1)°) and $[CuBr(PMePh_2)]_4$ (avg. distances: Cu-Br, 2.558(10)Å; Cu-P, 2.210(19)Å; Br-Cu-Br', 101.65(4)°; Cu-Br-Cu', 76.5(3)°). These complexes crystallized in space group C2/c and Aba2 with the 2-fold axis passing through two opposite faces of the cube relating atoms at opposite corners of those faces.

Coordination of copper atoms in the cubic complexes is tetrahedral (P-Cu-I, 98.9(2)-114.0(2)°; P-Cu-Br, 117.9(1)-120.7(1)°) with each copper atom bound to three halide atoms and an electron pair donating phosphorus atom of a tri-substituted phosphine ligand. These distances for Cu-X and Cu-P in both structures are normal and may be compared to those of the known copper(I) cubic clusters previously reported in the literature (Table I).

The Cu···Cu distances in the bromine cubic clusters averaged 3.038(14) Å while the Cu···Cu distance in the iodine counterparts averaged 2.946 Å. These distances for both copper(I) halide complexes are longer than those Cu···Cu distances believed to represent metal metal interaction (2.8 Å). Thus, excitation mechanisms involving only neighboring copper atoms may be ruled out.

Trialkyl phosphine ligands have been characterized according to the spatial requirements of the alkyl groups. A common measurement of steric bulk is C. A. Tolman's cone angle (θ) (Figure 6).[60] In other words, it is the angle at the

Figure 6. Cone Angle



M = metal
R = alkyl, aryl

metal atom of the cone swept out by the van der Waals radii of the groups attached to phosphorus (Table X). When θ is used to compare the complexes including one metal (the metal covalent radius is fixed) there are no gross distortions within the steric scale.

Varying the substituents on the phosphorus ligands causes dramatic changes in the behavior of the free ligands and of their transition metal complexes. Steric factors, particularly those due to bulky ligands, frequently dominate and influence the course of many reactions.

Tolman's concept can easily be translated to the solid state structures of the complexes prepared in this work. Crystallographically, it would appear that when the cone angle is greater, the angles L-M-X should display larger values while the X-Cu-X' angles should decrease in size. This was not observed structurally in the structures prepared or reprepared from literature. The L-M-X angles in the cubic clusters appear well within normal even as the cone angle increases from $PMePh_2$ to P(*m*-toly)$_3$. However attempts to prepare a cubic compound with P(*o*-toly)$_3$, in which copper is 4 coordinate, remain a problem.

Considering that this ligand has the largest cone angle, 194°, it is not surprising that this ligand formed a rhombohedron with copper(I) halide, in which copper is three coordinate, rather than a cube with four coordinate copper due to the increased steric bulk of this ligand.

Table VIII
Cone angles and pKa's of common phosphines

PHOSPHINE	Cone Angle(°)	pK_a*
$P(Me)_3$	118	8.65
$PhP(Me)_2$	122	6.5
$P(Et)_3$	132	8.69
$P(^nBu)_3$	132	8.43
$(Ph)_2PMe$	136	4.57
$P(Ph)_3$	145	2.73
$P(p\text{-}MeC_6H_4)_3$	145	3.84
$P(m\text{-}MeC_6H_4)_3$	165	3.30
$P(Cy)_3$	170	9.70
$P(^tBu)_3$	182	11.40
$P(o\text{-}MeC_6H_4)_3$	194	3.08

* -- The basicity of the free ligand, normally expressed as the pK_a value for the conjugate acid (HPR_3^+), provides a reasonable measure of the ligand's ability to donate sigma electrons to the metal.

Another illustration of Tolman's cone angle concept is the synthesis of rhombohedral motifs of the type: [1:1:1], [1:1:1.5] and [1:1:2]. The copper complex with the smallest cone angle prepared (136°), $Cu_2Br_2(PMePh_2)_3$, demonstrates that steric bulk is minimal, allowing the two copper(I) bromide molecules to complex with two methyldiphenylphosphine ligands. $[CuI(o\text{-toly})_3]_2$, shows that, sterically two *o*-tolylphosphine ligands bound to one four coordinate copper atom is prohibited because this complex possesses the largest cone angle. Finally, $Cu_2Br_2(P(m\text{-toly})_3)_3$ has a cone angle that lies halfway between the two other ligands. This structure demonstrates that one copper atom is four

coordinate with two phosphine ligands and the other copper atom is three coordinate bound to one phosphine ligand, representing a rhombohedron with coordination to a phosphine of intermediate size.

Within the group of $Cu_4X_4P_4$ complexes, there are no outstanding crystallographic differences between complexes with different symmetry elements present in their solid state forms.

Emission studies were carried out on all cubic clusters as well as their uncomplexed ligands, provided they were solids at room temperature. The study revealed that the pure ligands emitted only weakly in the 400-425nm region. The metal halide complex ordinarily shows observable emission.

The two cubic clusters containing a two-fold symmetry element emitted in the region between 575 and 615nm. When the symmetry element was a three-fold axis, emission shifted to lower wavelength 470 to 520nm. Emission was observed for all complexes containing iodide and was absent for any bromide complex except $[CuBrP(p\text{-toly})_3]_4$ which emitted at 490nm. The complexes showed very little shift of wavelength of maximum emission between room temperature and low temperature that showed increased intensity at low temperature. Emission from the uncomplexed tri-*p*-tolyphosphine ligand was ruled out because the complexes showed strong emission at wavelengths different from that of the pure ligand.

Variations in solvent, conditions, temperature often lead to different products. Because cubes, rhombohedra and chairs can display the same 1:1:1 stoichiometry (Cu:X:Ligand), the mixtures of starting materials offers no guarantee of the product formation. The emission observed might be from a mixture of products. All emission spectra showed single maxima and appeared free from contamination.

B. Rhombohedra

The second class of compounds studied was rhombohedra of the type $M_2X_2L_2$. Two new compounds, $Cu_2I_2(P(o\text{-tol})_3)_2\cdot[C_7H_8]$ and $Cu_2Br_2(P(m\text{-tol})_2)_3$ were prepared. The crystal containing tri-*o*-tolylphosphine crystallizes in the space group $P2_1/n$ and has one additional toluene molecule in the unit cell (Figure 19). An inversion center relates one half of the rhombohedron to the other. The copper atom is trigonal planar with a I-Cu-I' bond angle of 105.60(6)°. The Cu-I bond distance averaged 2.589(2)Å (Tables XXXVII - XLI). The Cu···Cu and I···I distances are 3.131 and 4.124 Å respectively. Emission was not observed for the *o*-toluene complex.

The second compound, $Cu_2Br_2(P(m\text{-tol})_2)_3$, crystallizes in P_1 bar space group with an internal 2-fold axis (Figure 14; Table XXVI). The Cu-P and Cu-Br distances averaged 2.236(5) and 2.495(3)Å. The Cu-Br-Cu' and Br-Cu-Br' angles are 73.99(9) and 105.84(9)°, respectively. Emission studies were not performed on this complex due to decomposition of the crystal upon exposure to air.

C. Monomers

The two monomeric $CuBr(Pcy_3)_2$ complexes are allotropes which arise upon crystallization (or preparation) from different solvents. Allotropes are different crystalline forms which differ only in their packing in the solid form. The form crystallized from hexane is found in space group C2/c with a 2-fold symmetry element within the monomeric form. In the solid the planes of the P_2CuBr groups are parallel (Figure 21). The Cu - Br and Cu - P distances are 2.390(2) and 2.260(9)Å, respectively. Emission from this complex occured at 390 nm at both low and room temperature studies.

The form crystallized from benzene is found in space group $P2_1/n$ with no symmetry element within the motif (Figure 22). The planes of the P_2CyBr groups

are found to be canted. Cu-Br and Cu-P distances averaged 2.384(6) and 2.282(8)Å, respectively. Emission is observed for both complexes at 385 nm and 375 nm. The effect of a 2-fold axes has no effect on the wavelength of maximum emission. The two fold axis does not impose forbiddenness upon transitions between molecular orbitals. The influence of packing on wavelength of maximum emission can therefore be ruled out.

D. Linked cubes

A previously unseen motif in the literature of copper halide complexes was prepared, $Cu_8I_8(P(Ph_2(p\text{-toly})))_6$. This compound crystallized in the P_1 bar crystallographic space group with a center of symmetry relating one cube to another (Figure 23). The cubes are linked by two copper iodide bonds. The Cu-I (avg. 2.690(4) Å) and Cu-P (avg. 2.252(7)Å) distances appear normal. The Cu-I-Cu', I-Cu-I' and I-Cu-P angles also are well within the expected angles for cubes. Cubes have been observed in the literature linked by corners of one cube to another but not by an edge[59]. This crystal was prepared in an attempt to prepare a cubic cluster of the type $[Cu_4X_4L_4]$. Cone angle analysis suggests that the target compound should exist.

E. Mixed Metal complex

Emitting copper halide and copper halide ligand species have been studied with variation of halide, and of ligand. While copper(II) has been seen to quench emission, these has been no investigation into mixed metal systems. Other metals besides copper(I) are known to form emitting complexes. Attempts were made to prepare mixed metal halide complexes to explore this area.

Durand et al[61] studied the possiblity of integrating zinc into copper(I) complexes. Copper(I) iodide and zinc(II) iodide were added to pyridine forming a mixed metal (Cu:Zn 50:50) pyridine iodide complex: $Cu(II)_{0.92}Zn(II)_{0.08}(pyridine)_4I_2$•pyridine (Figure 25). Tetrapyridinodiiodo-

copper(II) zinc(II) pyridine is an octahedral complex, in which the metal site is six coordinated, crystallizing in the crystallographic space group Ccca. There are two long M···I bonds of 3.460(5) Å where the I···M···I are parallel to the A axis with a 5.392 Å separation between iodide atoms of adjacent groups. This complex did not emit under the influence of ultra-violet radiation.

F. Conclusion

The copper halide complexes which have been synthesized display a variety of properties and structural motifs. The structures prepared are similar to CuXL (X = Br, I) complexes observed in the literature, mainly cubic clusters and rhombohedra. This study has found emission between 500-615nm for iodide cubic clusters and 490nm for $[CuBrP(p\text{-toly})_3]_4$ which may be correlated with symmetry elements present within the complexes in room temperature single crystal X-ray studies. *Ab initio* calculations are under way to probe the nature of the transitions leading to emission.

Table IX

EXPERIMENTAL COPPER(I) HALIDE PHOSPHINE COMPLEXES*

Compound	Distances (Å) M-X	M-L	M···M	X···X	Angles(°) M-X-M	X-M-X	L-M-X
$CuBr(PMePh_2)]_4$	2.481(14) -2.625(10)	2.192(19) -2.228(20)	3.038	3.963	72.4(3) -82.5(3)	96.1(3) -104.9(9)	100.0(5) -111.8(6)
$CuI(PMe_2Ph)]_4$	2.628(2) -2.780(3)	2.242(8) -2.250(7)	2.826	4.579	61.9(1) -66.1(1)	108.7(1) -114.7(1)	98.8(2) -113.9(2)
$CuIP(p\text{-tolyl})_3]_4$	2.674(3) -2.705(3)	2.239(10) -2.253(6)	3.152	4.280	70.10(12) -71.91(9)	105.81(10) -107.45(10)	111.0(2) -114.0(2)
$[CuBrP(p\text{-tolyl})_3]_4$	2.547(3) -2.567(3)	2.221(6) 2.224(8)	3.230	3.902	78.6(1) -79.8(1)	99.4(1) -100.7(1)	117.9(1) -120.7(1)
$[CuIP(m\text{-tolyl})_3]_4$	2.706(9) -2.754(6)	2.205(26) -2.229(15)	2.923	4.249	75.1(3) -83.7(2)	94.8(3) -103.3(2)	115.4(4) -121.8(2)
$[CuIP(o\text{-tolyl})_3]_2$	2.530(2)	2.233(3) -2.647(2)	3.131	4.124	74.40(6)	105.60(6)	117.54(10) -136.77(11)
$[Cu_2Br_2(P(m\text{-tolyl})_3]_3]$	2.386(3) -2.611()	2.201(5) -2.256(5)	3.007(3)	4.124	73.86(9) -74.11(9)	99.26(9) -112.42(10)	100.74(14) -108.92(14)
$[CuBr(P(C_6H_{11})_3)_2]$	2.390(2)	2.250(8) 2.270(11)					112.3(3) -112.4(3)
$[CuBr(P(C_6H_{11})_3)_2]$**	2.384(6)	2.276(8) 2.287(8)					107.3(3) -115.7(3)

* -- ranges are given where appropriate
** - complexed in benzene

Table X

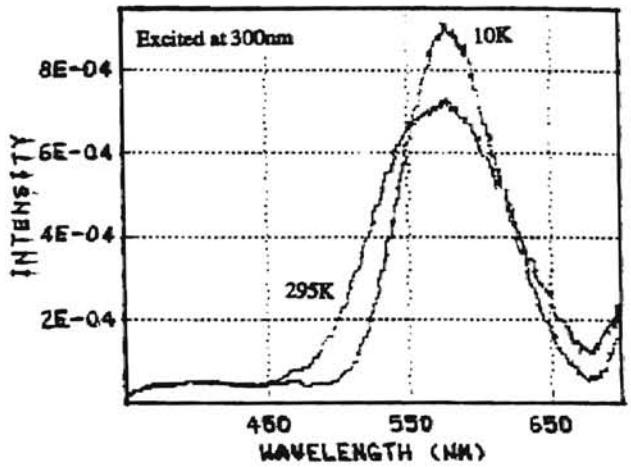
SYMMETRY AND EMISSION OF COPPER(I) HALIDE COMPOUNDS WITH PHOSPHORUS LIGANDS

Compound	Space Group	Symmetry	λ_{em} (nm) LT	HT
CUBES:				
$[CuIP(MePh_2)]_4$	P-1	2	577	577
$[CuBrP(MePh_2)]_4$	Aba2	2	---	---
$[CuIP(Me_2Ph)]_4$	C2/c	2	615	615
$[CuBrP(Me_2Ph)]_4$	C2/c	2	---	---
$P(C_6H_5)_3$	---	---	425	---
$[CuIPPh_3]_4$	$P2_1/n$	1	540	573
$[CuBrPPh_3]_4$	Pbcn	2	---	---
P(*m*-toluene)$_3$	---	---	---	---
$[CuIP(C_6H_4Me\text{-}m)_3]_4$	I-43d	3	---	--
P(*p*-toluene)$_3$	---	---	400	---
$[CuIP(C_6H_4Me\text{-}p)_3]_4$	R-3	3	520	520
$[CuBrP(C_6H_4Me\text{-}p)_3]_4$	R-3	3	490	490

Table X (Continued)

Compound	Space Group	Symmetry	λ_{em} (nm) LT	HT
RHOMBS:				
P(*o*-toluene)$_3$	---	---	---	---
[CuIP(C_6H_4Me-*o*)$_3$]$_2$ •C_6H_5Me	$P2_1/n$	2	---	---
[CuBrP($MePh_2$)]$_2$	P-1	1	---	---
[CuIP(C_6H_{11})$_3$]$_2$	P_1	2	375	375
[1:1:2] monomers:				
P(cyclohexane)$_3$	---	---	---	---
[CuBr(PCy_3)$_2$] from hexane	C2/c	2	460	460
[CuBr(PCy_3)$_2$]* from benzene	$P2_1/n$	none	400	---

[CuIP(MePh2)]4



[CuBrP(MePh2)]4

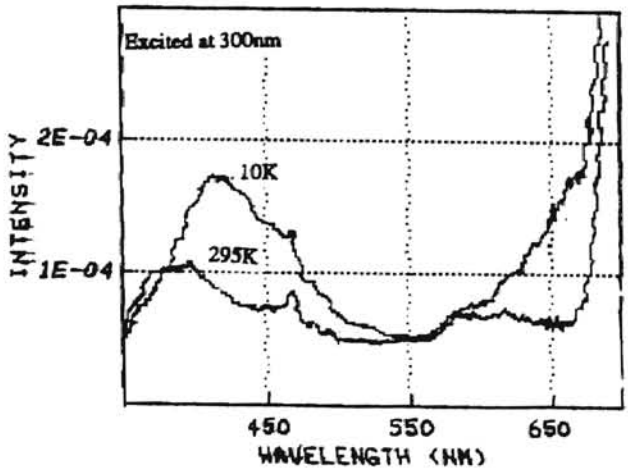


Figure 7. Emisson Spectra of [CuI(PMePh2)]4 and [CuBr(PMePh2)]4

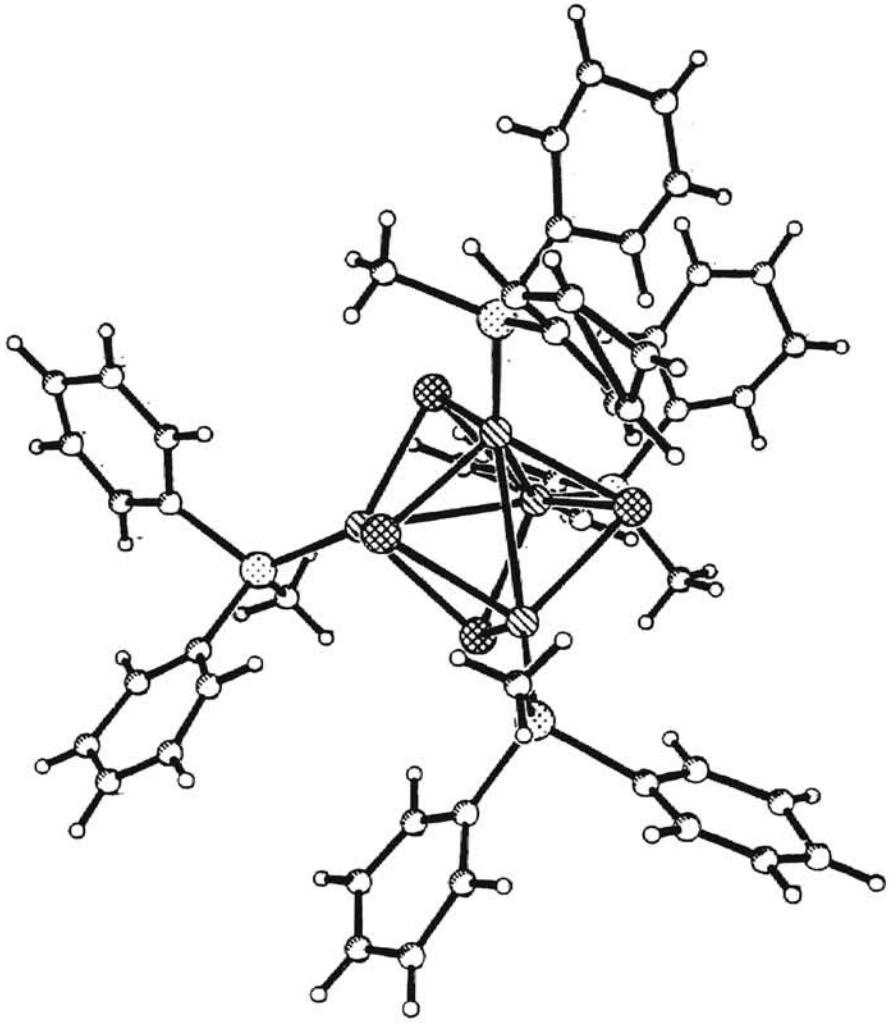


Figure 8. Projection view of $[CuBr(PMePh_2)]_4$

TABLE XI

CRYSTAL DATA FOR [CuBrP(MePh2)]4

Formula	$Cu_2Br_2P_2C_{26}H_{26}$
MWT	687.30
a	18.552(7) Å
b	18.612(8)
c	15.603(6)
α	90.0°
β	90.0
γ	90.0
V	5388(4) $Å^3$
F (000)	2720
μMoK_a	4.677 cm^{-1}
λMoK_a	0.71073 Å
D_{calc}	1.695 Mg m^{-3}
Z	8
Independent Refl.	1348
Obs. Refl. ($F>4.0\sigma(F)$)	864
R/R_w	7.49/7.39%
Space Group	Aba2
Octants Meas.	$-1 \leq h \leq 24, -24 \leq k \leq 1$
	$-1 \leq l \leq 20$

TABLE XII

POSITIONAL PARAMETERS FOR
$[CuBrP(MePh_2)]_4$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br(1)	953(3)	4463(3)	2069
Br(2)	357(3)	5976(3)	3865(5)
Cu(2)	832(4)	4602(4)	3695(7)
Cu(1)	439(4)	5686(4)	2316(7)
P(2)	1775(8)	4630(8)	4578(14)
P(1)	825(9)	6604(9)	1566(12)
C(31)	2341(23)	5415(22)	4522(24)
C(11)	430(28)	7510(22)	1890(35)
C(21)	1873(37)	6780(38)	1592(32)
C(22)	2265(41)	6169(26)	1814(59)
C(23)	2798(54)	6439(34)	1948(42)
C(24)	3309(23)	6974(25)	1662(48)
C(25)	2782(23)	7475(45)	1589(34)
C(26)	2072(49)	7416(39)	1679(56)
C(41)	2542(36)	3936(27)	4500(32)
C(42)	3273(23)	3953(22)	4717(28)
C(43)	3557(45)	3340(25)	4522(40)
C(44)	3420(17)	2763(21)	4135(27)
C(45)	2763(42)	2818(33)	3806(58)
C(46)	2291(35)	3372(41)	4020(37)
C(51)	715(20)	6569(36)	412(29)
C(52)	754(22)	5924(35)	-8(28)
C(53)	627(24)	5814(33)	-835(27)
C(54)	598(30)	6383(29)	-1354(50)
C(55)	544(34)	7113(49)	-1021(73)
C(56)	678(40)	7084(27)	-217(60)
C(61)	1510(58)	4453(30)	5694(49)
C(62)	848(45)	4329(51)	6000(53)
C(63)	663(28)	4299(28)	6807(46)
C(64)	1214(47)	4324(36)	7382(32)
C(65)	1882(28)	4355(30)	7172(31)
C(66)	1998(35)	4454(33)	6303(38)

TABLE XIII

HYDROGEN POSITIONAL PARAMETERS FOR
$[CuBrP(MePh_2)]_4$

ATOM	x	y	z
H(31A)	2725	5372	4931
H(31B)	2539	5457	3956
H(31C)	2060	5835	4650
H(11A)	615	7888	1534
H(11B)	-87	7502	1852
H(11C)	571	7592	2473
H(22A)	2063	5698	1895
H(23A)	3106	6042	2088
H(24A)	3819	7046	1722
H(25A)	2984	7945	1508
H(26A)	1764	7813	1539
H(42A)	3457	4363	5019
H(43A)	4050	3348	4710
H(44A)	3729	2360	4021
H(45A)	2579	2408	3504
H(46A)	1798	3364	3832
H(52A)	807	5504	344
H(53A)	623	5345	-1092
H(54A)	542	6334	-1963
H(55A)	491	7533	-1372
H(56A)	682	7553	40
H(62A)	480	4337	5568
H(63A)	165	4263	6967
H(64A)	1084	4280	7975
H(65A)	2250	4347	7605
H(66A)	2496	4489	6143

TABLE XIV

ANISOTROPIC THERMAL PARAMETERS FOR
$[CuBrP(MePh_2)]_4$

ATOM	U11	U22	U33	U12	U13	U23
Br(1)	46(3)	84(5)	64(5)	-4(4)	-1(4)	-2(5)
Br(2)	64(4)	84(5)	52(4)	-11(4)	-5(4)	-2(5)
Cu(2)	55(5)	107(7)	81(7)	6(5)	-7(5)	13(6)
Cu(1)	90(7)	107(7)	98(8)	-4(6)	8(6)	7(6)
P(2)	31(8)	55(12)	133(20)	1(9)	-18(11)	64(14)
P(1)	76(13)	41(10)	70(12)	11(10)	-10(12)	9(9)
C(31)	55(34)	114(45)	49(34)	32(33)	-22(27)	149(33)
C(11)	143(53)	21(30)	97(57)	-96(36)	-10(52)	16(35)
C(21)	176(68)	182(66)	0(27)	218(60)	-62(38)	-31(38)
C(22)	218(87)	0(23)	424(152)	-98(39)	-26(86)	-149(60)
C(23)	520(153)	64(48)	122(69)	-213(75)	-167(87)	-29(50)
C(24)	0(23)	37(32)	301(113	-52(23)	120(42)	-54(49)
C(25)	25(26)	292(104)	88(43)	-50(42)	137(31)	-114(50)
C(26)	289(118)	95(61)	263(135	184(73)	143(102	-44(75)
C(41)	127(57)	35(33)	0(27)	9(43)	-61(33)	0(31)
C(42)	48(28)	34(31)	48(31)	14(26)	-92(27)	-78(26)
C(43)	482(134)	55(39)	98(59)	259(65)	-36(70)	-51(40)
C(44)	24(17)	101(34)	58(33)	156(24)	-65(23)	-52(29)
C(45)	200(69)	77(61)	124(78)	-38(55)	14(76)	-71(65)
C(46)	105(52)	166(72)	0(29)	71(56)	40(37)	40(46)
C(51)	0(22)	251(69)	41(33)	-100(36)	20(22)	-185(44)
C(52)	10(28)	178(63)	0(28)	28(35)	14(24)	-26(35)
C(53)	48(31)	112(56)	0(28)	45(34)	46(24)	-37(30)
C(54)	97(53)	79(45)	126(68)	107(45)	107(54)	77(51)
C(55)	45(55)	243(104)	434(147	-48(60)	-108(79)	370(112)
C(56)	186(83)	0(35)	206(99)	19(38)	34(78)	91(58)
C(61)	370(13)	0(27)	103(72)	-47(63)	-167(88)	92(41)
C(62)	157(84)	264(117)	85(61)	-96(76)	159(65)	20(66)
C(63)	30(29)	59(45)	109(67)	-29(33)	-1(42)	-50(48)
C(64)	289(10)	230(75)	0(32)	-240(78)	51(50)	-111(44)
C(65)	70(37)	107(53)	20(30)	3(42)	-38(30)	84(38)
C(66)	133(51)	115(54)	65(39)	-106(44)	-31(40)	140(41)

The anisotropic displacement exponet takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE XV

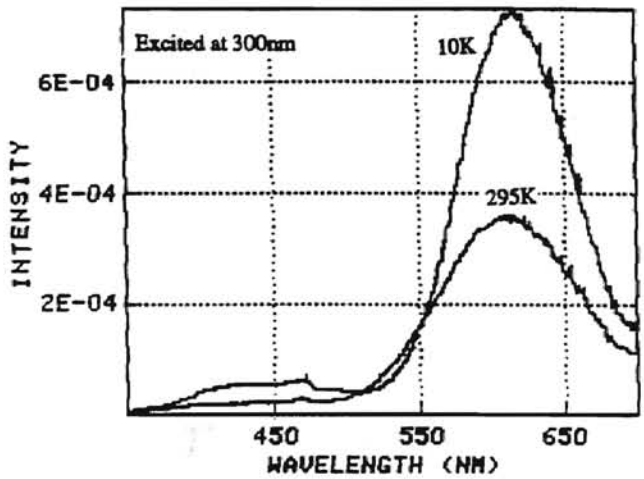
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[CuBrP(MePh_2)]_4$

Br(1)-Cu(2)	2.560 (11)	Cu(2)-Br(1)-Cu(1)	73.8(3)
Br(1)-Cu(1)	2.498 (11)	Cu(2)-Br(1)-Cu(1A)	77.2(3)
Br(1)-Cu(1A)	2.625 (10)	Cu(1)-Br(1)-Cu(1A)	72.4(3)
Br(2)-Cu(2)	2.717 (10)	Cu(2)-Br(2)-Cu(1)	71.4(3)
Br(2)-Cu(1)	2.481 (14)	Cu(2)-Br(2)-Cu(2A)	82.5(3)
Br(2)-Cu(2A)	2.468 (9)	Cu(1)-Br(2)-Cu(2A)	81.7(4)
Cu(2)-Cu(1)	3.038 (14)	Br(1)-Cu(2)-Br(2)	102.7(4)
Cu(2)-P(2)	2.228 (20)	Br(1)-Cu(2)-Cu(1)	52.2(3)
Cu(2)-Br(2A)	2.468 (9)	Br(2)-Cu(2)-Cu(1)	50.7(3)
Cu(1)-P(1)	2.192 (19)	Br(1)-Cu(2)-P(2)	123.2(6)
Cu(1)-Br(1A)	2.625 (10)	Br(2)-Cu(2)-P(2)	100.0(5)
Cu(1)-Cu(1A)	3.028 (17)	Cu(1)-Cu(2)-P(2)	127.7(5)
P(2)-C(31)	1.801 (44)	Br(1)-Cu(2)-Br(2A)	98.1(4)
P(2)-C(41)	1.925 (61)	Br(2)-Cu(2)-Br(2A)	96.3(3)
P(2)-C(61)	1.839 (83)	Cu(1)-Cu(2)-Br(2A)	98.7(3)
P(1)-C(11)	1.906 (46)	P(2)-Cu(2)-Br(2A)	130.2(7)
P(1)-C(21)	1.972 (70)	Br(1)-Cu(1)-Br(2)	111.8(4)
P(1)-C(51)	1.813 (49)	Br(1)-Cu(1)-Cu(2)	54.0(3)
C(21)-C(22)	1.395 (90)	Br(2)-Cu(1)-Cu(2)	58.0(3)
C(21)-C(23)	1.913 (114)	Br(1)-Cu(1)-P(1)	120.2(6)
C(21)-C(26)	1.246 (101)	Br(2)-Cu(1)-P(1)	111.8(6)
C(22)-C(23)	1.130 (116)	Cu(2)-Cu(1)-P(1)	144.8(6)
C(23)-C(24)	1.444 (96)	Br(1)-Cu(1)-Br(1A)	104.9(3)
C(23)-C(25)	2.007 (104)	Br(2)-Cu(1)-Br(1A)	96.1(3)
C(24)-C(25)	1.355 (79)	Cu(2)-Cu(1)-Br(1A)	105.7(3)
C(25)-C(26)	1.329 (100)	P(1)-Cu(1)-Br(1A)	109.0(6)
C(41)-C(42)	1.397 (78)	Br(1)-Cu(1)-Cu(1A)	55.7(3)
C(41)-C(46)	1.371 (87)	Br(2)-Cu(1)-Cu(1A)	98.6(2)
C(42)-C(43)	1.292 (69)	Cu(2)-Cu(1)-Cu(1A)	64.5(3)
C(43)-C(44)	1.258 (65)	P(1)-Cu(1)-Cu(1A)	146.4(6)
C(44)-C(45)	1.326 (88)	Br(1A)-Cu(1)-Cu(1A)	51.9(3)
C(45)-C(46)	1.393 (100)	Cu(2)-P(2)-C(31)	116.5(16)
C(51)-C(52)	1.369 (86)	Cu(2)-P(2)-C(41)	121.7(19)
C(51)-C(56)	1.375 (95)	C(31)-P(2)-C(41)	96.4(23)
C(52)-C(53)	1.329 (62)	Cu(2)-P(2)-C(61)	111.8(33)
C(53)-C(54)	1.334 (85)	C(31)-P(2)-C(61)	110.3(28)
C(54)-C(55)	1.458 (109)	C(41)-P(2)-C(61)	97.9(31)
C(55)-C(56)	1.280 (146)	Cu(1)-P(1)-C(11)	115.0(18)
C(61)-C(62)	1.337 (133)	Cu(1)-P(1)-C(21)	116.2(20)
C(61)-C(66)	1.313 (113)	C(11)-P(1)-C(21)	103.1(26)
C(62)-C(63)	1.305 (109)	Cu(1)-P(1)-C(51)	117.7(21)
C(63)-C(64)	1.362 (95)	C(11)-P(1)-C(51)	104.6(27)

Table XV (Continued)

C(64)-C(65)	1.284 (99)	C(21)-P(1)-C(51)	97.9(21)
C(65)-C(66)	1.385 (76)	P(1)-C(21)-C(22)	112.5(50)
		P(1)-C(21)-C(23)	146.6(44)
		C(22)-C(21)-C(23)	35.8(39)
		P(1)-C(21)-C(26)	116.9(61)
		C(22)-C(21)-C(26)	126.4(71)
		C(23)-C(21)-C(26)	91.0(59)
		C(21)-C(22)-C(23)	98.0(58)
		C(21)-C(23)-C(22)	46.2(49)
		C(21)-C(23)-C(24)	105.7(46)
		C(22)-C(23)-C(24)	145.5(76)
		C(21)-C(23)-C(25)	65.6(34)
		C(22)-C(23)-C(25)	111.3(64)
		C(24)-C(23)-C(25)	42.4(27)
		C(23)-C(24)-C(25)	91.6(50)
		C(23)-C(25)-C(24)	46.0(44)
		C(23)-C(25)-C(26)	84.6(56)
		C(24)-C(25)-C(26)	130.4(73)
		C(21)-C(26)-C(25)	111.2(76)
		P(2)-C(41)-C(42)	133.3(38)
		P(2)-C(41)-C(46)	107.3(47)
		C(42)-C(41)-C(46)	118.6(52)
		C(41)-C(42)-C(43)	108.6(50)
		C(42)-C(43)-C(44)	141.5(72)
		C(43)-C(44)-C(45)	107.8(53)
		C(44)-C(45)-C(46)	122.8(67)
		C(41)-C(46)-C(45)	118.9(62)
		P(1)-C(51)-C(52)	120.1(44)
		P(1)-C(51)-C(56)	133.6(52)
		C(52)-C(51)-C(56)	105.8(47)
		C(51)-C(52)-C(53)	126.2(55)
		C(52)-C(53)-C(54)	118.3(59)
		C(53)-C(54)-C(55)	121.7(74)
		C(54)-C(55)-C(56)	107.3(76)
		C(51)-C(56)-C(55)	137.6(65)
		P(2)-C(61)-C(62)	127.9(72)
		P(2)-C(61)-C(66)	120.1(71)
		C(62)-C(61)-C(66)	112.0(70)
		C(61)-C(62)-C(63)	126.4(78)
		C(62)-C(63)-C(64)	115.9(61)
		C(63)-C(64)-C(65)	124.0(53)
		C(64)-C(65)-C(66)	113.9(51)
		C(61)-C(66)-C(65)	127.0(66)

[CuIP(Me2Ph)]4



[CuBrP(Me2Ph)]4

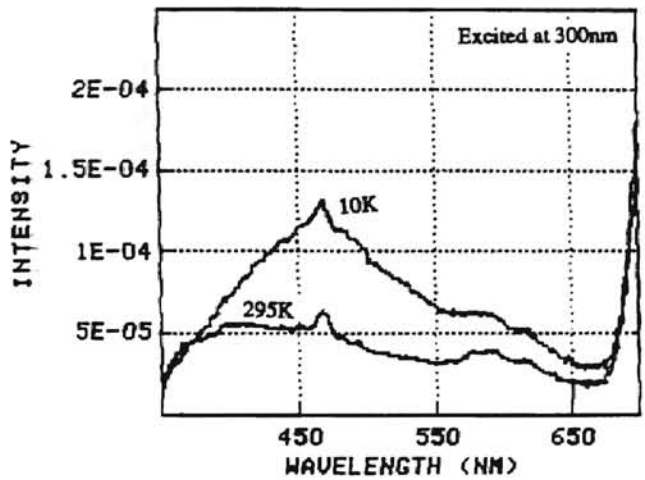


Figure 9. Emisson Spectra of [CuI(PMe2Ph)]4 and [CuBr(PMe2Ph)]4

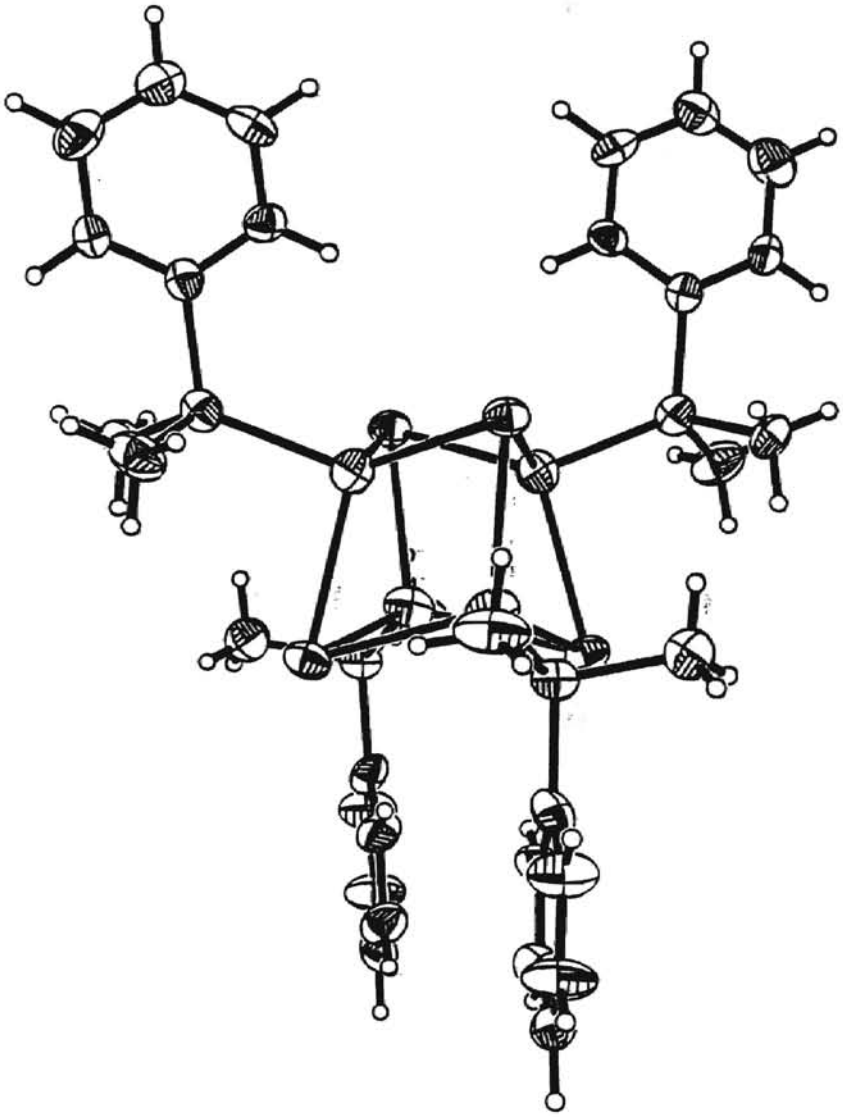


Figure 10. Projection view of [CuI(PMe2Ph)]4

TABLE XVI

CRYSTAL DATA FOR $[CuIP(Me_2Ph)]_4$

Formula	$CuIPC_8H_{11}$
MWT	292.1
a	25.897(2) Å
b	11.783(1)
c	19.337(1)
α	90.0°
β	113.89(1)
γ	90.0
V	4392.4(6) $Å^3$
F (000)	2496
μMoK_a	35.40 cm^{-1}
λMoK_a	0.71073 Å
D_{calc}	1.987 g cm^{-3}
Z	18
Independent Refl.	2521
Obs. Refl. ($F>9.0\sigma(F)$)	1234
R/R_w	4.8/5.7%
Space Group	C2/c
Octants Meas.	$-1 \leq h \leq 24, -1 \leq k \leq 11,$ $-18 \leq l \leq 14$

TABLE XVII

POSITIONAL PARAMETERS FOR
$[CuIP(Me_2Ph)]_4$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.0541(1)	0.0511(1)	0.3947(1)
I2	-0.0969(1)	-0.2353(1)	0.2212(1)
Cu1	0.0379(1)	-0.1755(2)	0.3452(2)
Cu2	0.0645(1)	-0.0074(3)	0.2681(2)
P1	0.0889(3)	-0.2514(5)	0.4847(4)
P2	0.1649(3)	0.0645(5)	0.3190(4)
C10	0.0864(10)	-0.4011(19)	0.4945(15)
C11	0.0969(12)	-0.4582(23)	0.5662(16)
C12	0.0935(14)	-0.5709(23)	0.5699(19)
C13	0.0841(11)	-0.6386(22)	0.5056(21)
C14	0.0708(11)	-0.5882(23)	0.4327(20)
C15	0.0717(10)	-0.4693(21)	0.4246(15)
C40	0.1732(12)	0.2199(17)	0.3161(13)
C41	0.1177(11)	0.2876(19)	0.2818(12)
C42	0.1246(14)	0.4021(20)	0.2815(14)
C45	0.2341(11)	0.2694(21)	0.3496(15)
C43	0.1848(15)	0.4496(22)	0.3139(14)
C44	0.2403(15)	0.3875(24)	0.3487(17)
C20	0.0541(13)	-0.1922(19)	0.5330(16)
C30	0.1795(10)	-0.2217(20)	0.5732(16)
C50	0.1942(12)	0.0070(20)	0.2633(16)
C60	0.2356(9)	0.0326(18)	0.4400(13)

TABLE XVIII

HYDROGEN POSITIONAL PARAMETERS FOR
$[CuIP(Me_2Ph)]_4$

ATOM	x	y	z
H11A	1064	-4127	6148
H12A	1003	-6051	6205
H13A	844	-7198	5099
H14A	624	-6349	3853
H15A	609	-4349	3712
H41A	750	2526	2579
H42A	854	4489	2578
H43A	1877	5307	3129
H44A	2822	4231	3704
H45A	2734	2224	3744
H20A	770	-2263	5924
H20B	616	-1116	5405
H20C	52	-2075	4919
H50A	2371	420	2885
H30A	1979	-2569	6305
H30B	2040	-2490	5552
H30C	1849	-1409	5814
H50B	2010	-732	2749
H50C	1600	203	1975
H60A	2777	649	4599
H60B	2267	620	4775
H60C	2401	-485	4463

TABLE XIX

ANISOTROPIC THERMAL PARAMETERS FOR
$[CuIP(Me_2Ph)]_4$

ATOM	U11	U22	U33	U12	U13	U23
I1	70(1)	50(1)	56(1)	-2(1)	43(1)	-9(1)
I2	74(1)	52(1)	70(1)	-10(1)	54(1)	-1(1)
Cu1	96(2)	62(2)	56(2)	9(2)	53(2)	8(2)
Cu2	65(2)	69(2)	75(2)	-4(2)	48(2)	0(2)
P1	69(4)	50(4)	47(3)	0(3)	40(3)	-1(3)
P2	61(4)	63(4)	59(4)	7(3)	44(3)	7(3)
C10	58(14)	68(16)	51(14)	-21(12)	36(13)	-29(14)
C11	142(24)	64(21)	70(17)	2(16)	83(18)	11(14)
C12	165(28)	52(21)	109(22)	-3(17)	112(22)	11(17)
C13	66(16)	65(18)	116(22)	10(14)	66(17)	22(20)
C14	93(19)	79(23)	99(21)	-20(16)	74(18)	-28(17)
C15	76(17)	58(18)	68(17)	-11(13)	42(14)	18(14)
C40	49(13)	59(15)	48(13)	3(14)	35(11)	4(12)
C41	55(15)	49(17)	45(13)	-6(13)	30(12)	-6(11)
C42	79(19)	52(19)	64(15)	24(15)	50(15)	9(13)
C43	73(18)	71(18)	49(15)	-8(19)	31(15)	4(14)
C44	84(22)	88(24)	89(19)	-20(18)	63(18)	4(17)
C45	43(15)	63(19)	82(17)	7(13)	35(13)	11(13)
C20	166(25)	58(17)	111(20)	-7(17)	117(20)	-10(15)
C30	75(18)	82(20)	97(20)	3(15)	42(16)	13(16)
C50	112(20)	76(18)	118(20)	27(16)	95(18)	15(15)
C60	56(14)	67(17)	63(14)	18(12)	23(12)	27(13)

The anisotropic displacement exponet takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE XX

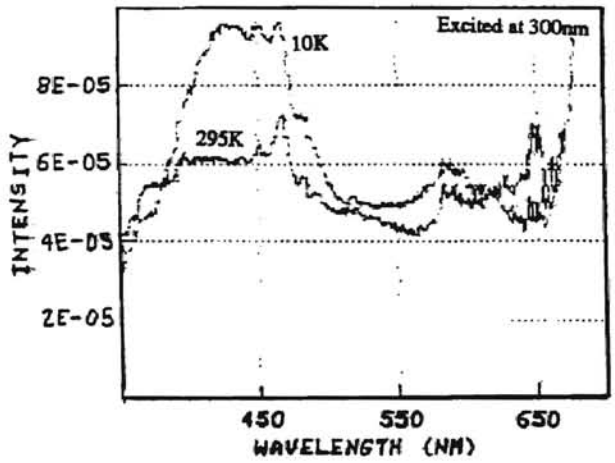
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[CuIP(Me_2Ph)]_4$

I1-Cu1	2.773 (3)	Cu1-I1-Cu2	61.9(1)
I1-Cu2	2.726 (5)	Cu1-I1-Cu2A	63.1(1)
I1-Cu2A	2.628 (2)	Cu2-I1-Cu2A	66.1(1)
I2-Cu1	2.692 (3)	Cu1-I2-Cu1A	62.6(1)
I2-Cu1A	2.664 (5)	Cu1-I2-Cu2A	62.2(1)
I2-Cu2A	2.780 (3)	Cu1A-I2-Cu2A	62.6(1)
Cu1-Cu2	2.828 (5)	I1-Cu1-I2	111.5(1)
Cu1-P1	2.250 (7)	I1-Cu1-Cu2	58.3(1)
Cu1-I2A	2.664 (5)	I2-Cu1-Cu2	110.0(1)
Cu1-Cu1A	2.784 (6)	I1-Cu1-P1	97.8(2)
Cu1-Cu2A	2.828 (4)	I2-Cu1-P1	109.8(2)
Cu2-P2	2.242 (8)	Cu2-Cu1-P1	139.1(2)
Cu2-I1A	2.628 (2)	I1-Cu1-I2A	114.7(1)
Cu2-I2A	2.780 (3)	I2-Cu1-I2A	108.7(1)
Cu2-Cu1A	2.828 (4)	Cu2-Cu1-I2A	60.7(1)
Cu2-Cu2A	2.922 (8)	P1-Cu1-I2A	113.9(2)
P1-C10	1.780 (23)	I1-Cu1-Cu1A	105.5(1)
P1-C20	1.818 (39)	I2-Cu1-Cu1A	58.2(1)
P1-C30	1.787 (19)	Cu2-Cu1-Cu1A	60.5(1)
P2-C40	1.849 (22)	P1-Cu1-Cu1A	156.4(2)
P2-C60	1.801 (17)	I2A-Cu1-Cu1A	59.2(2)
P2-C50	1.813 (39)	I1-Cu1-Cu2A	56.0(1)
C41-C40	1.366 (35)	I2-Cu1-Cu2A	60.4(1)
C41-C42	1.361 (33)	Cu2-Cu1-Cu2A	62.2(2)
C15-C10	1.390 (41)	P1-Cu1-Cu2A	134.7(3)
C15-C14	1.412 (37)	I2A-Cu1-Cu2A	110.8(2)
C40-C45	1.372 (39)	Cu1A-Cu1-Cu2A	60.5(1)
C11-C10	1.395 (45)	I1-Cu2-Cu1	59.9(1)
C11-C12	1.336 (38)	I1-Cu2-P2	106.9(2)
C42-C43	1.354 (48)	Cu1-Cu2-P2	130.7(2)
C45-C44	1.402 (38)	I1-Cu2-I1A	105.8(1)
C43-C44	1.328 (46)	Cu1-Cu2-I1A	108.3(1)
C13-C12	1.356 (53)	P2-Cu2-I1A	120.8(2)
C13-C14	1.346 (55)	I1-Cu2-I2A	112.5(1)
		Cu1-Cu2-I2A	56.7(1)
		P2-Cu2-I2A	97.4(2)
		I1A-Cu2-I2A	113.3(1)
		I1-Cu2-Cu1A	105.6(2)
		Cu1-Cu2-Cu1A	59.0(1)
		P2-Cu2-Cu1A	144.9(3)
		I1A-Cu2-Cu1A	61.0(1)

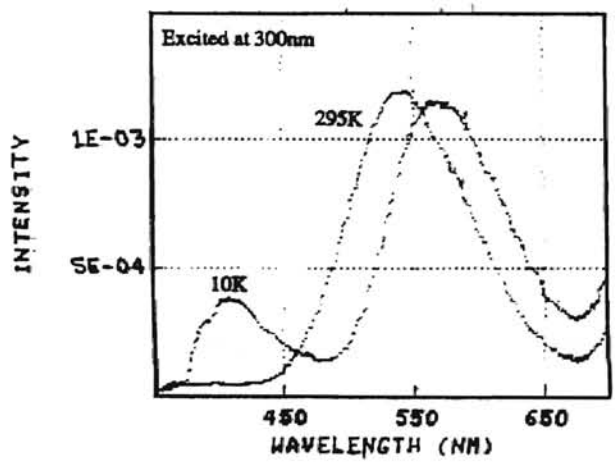
Table XX (Continued)

I2A-Cu2-Cu1A	57.4(1)
I1-Cu2-Cu2A	55.3(1)
Cu1-Cu2-Cu2A	58.9(1)
P2-Cu2-Cu2A	155.6(2)
I1A-Cu2-Cu2A	58.6(1)
I2A-Cu2-Cu2A	104.9(1)
Cu1A-Cu2-Cu2A	58.9(1)
Cu1-P1-C10	119.2(9)
Cu1-P1-C20	111.6(7)
C10-P1-C20	105.0(15)
Cu1-P1-C30	114.5(11)
C10-P1-C30	102.2(10)
C20-P1-C30	102.5(13)
Cu2-P2-C40	119.0(9)
Cu2-P2-C60	111.5(10)
C40-P2-C60	102.0(9)
Cu2-P2-C50	114.8(8)
C40-P2-C50	104.4(14)
C60-P2-C50	103.2(12)
C40-C41-C42	118.8(26)
C10-C15-C14	118.7(29)
P2-C40-C41	119.2(20)
P2-C40-C45	121.8(19)
C41-C40-C45	119.1(21)
C10-C11-C12	123.8(31)
P1-C10-C15	118.3(22)
P1-C10-C11	126.0(22)
C15-C10-C11	115.7(22)
C41-C42-C43	121.4(27)
C40-C45-C44	121.5(25)
C42-C43-C44	122.0(26)
C45-C44-C43	117.2(30)
C12-C13-C14	117.7(27)
C11-C12-C13	120.9(37)
C15-C14-C13	122.8(31)

PPh_3



$[CuIP(Ph_3)]_4$



$[CuBrP(Ph_3)]_4$

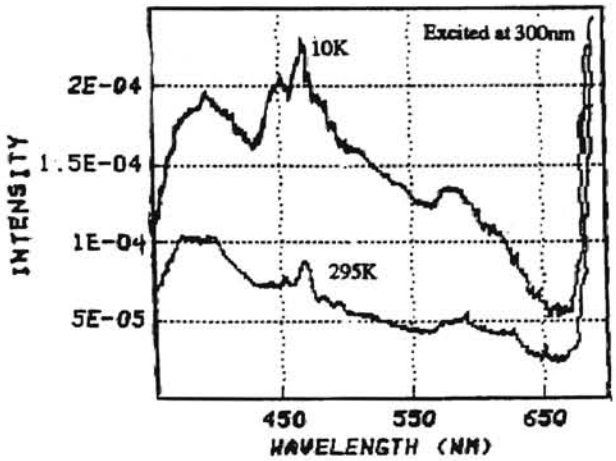
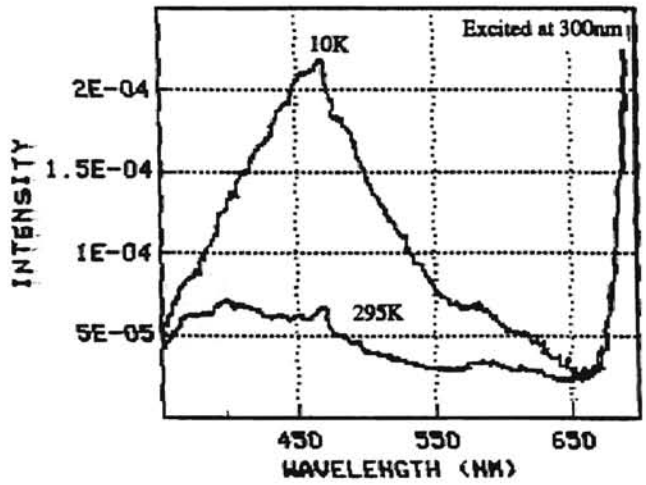


Figure 11. Emisson Spectra of PPh_3, $[CuI(PPh_3)]_4$ and $[CuBr(PPh_3)]_4$

P(*m*-tol)$_3$



[CuIP(*m*-tol)$_3$]$_4$

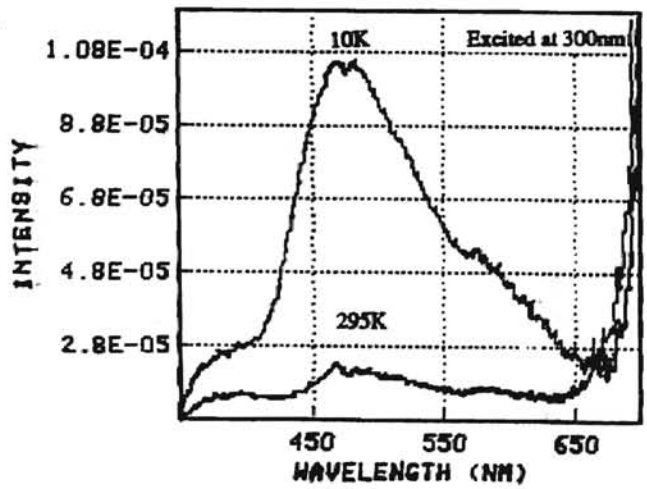


Figure 12. Emisson Spectra of P(m-tolyl)$_3$ and [CuIP(C$_6$H$_4$Me-*m*)$_3$]$_4$

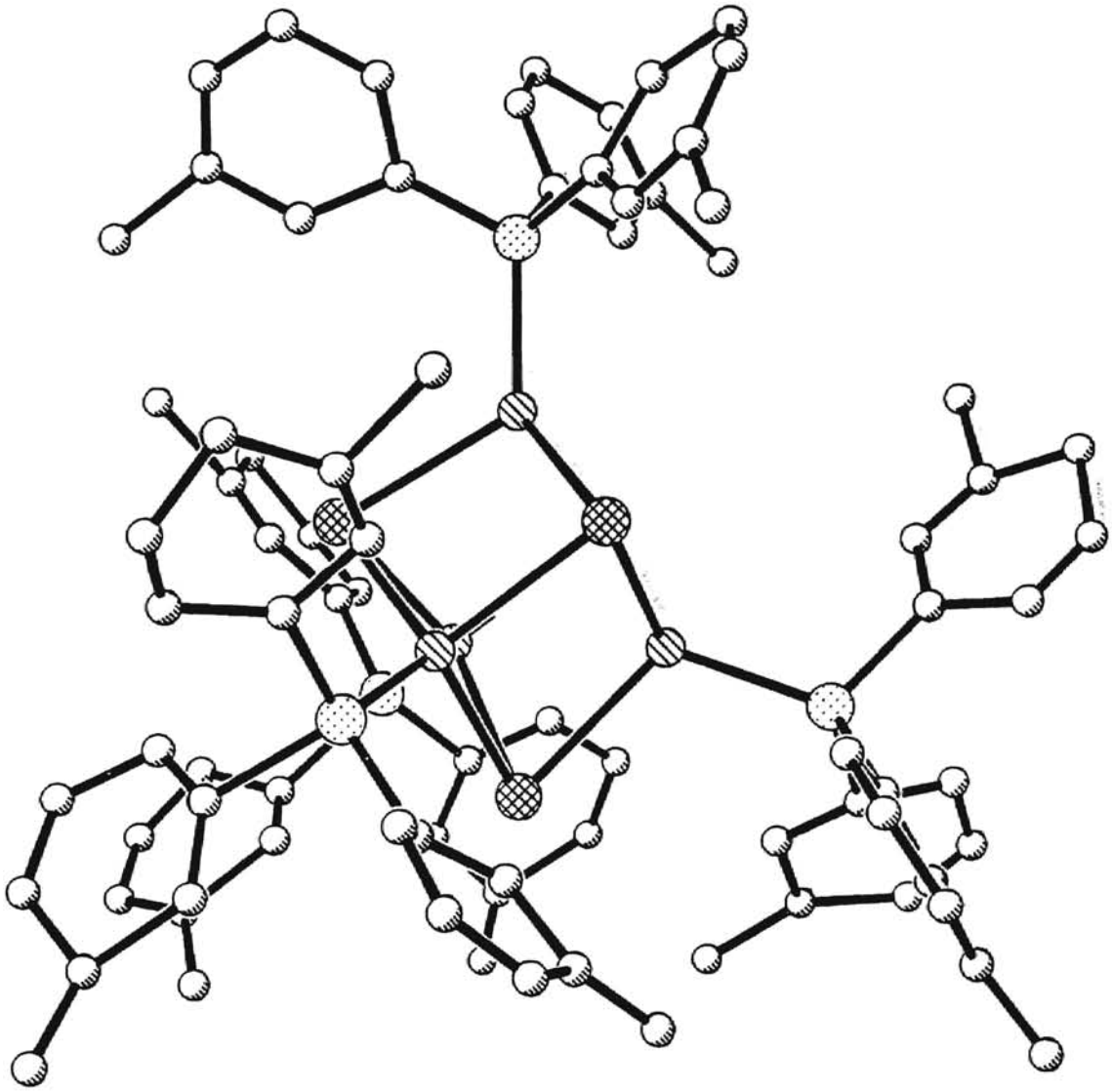


Figure 13. Projection view of [CuIP(C_6H_4Me-*m*)$_3$]$_4$

TABLE XXI

CRYSTAL DATA FOR [CuIP(C_6H_4Me-*m*)$_3$]$_4$

Formula	$Cu_4I_4P_4C_{81}H_{66}$
MWT	1925.0
a	31.868(3) Å
b	31.868(3)
c	31.868(3)
α	90.0°
β	90.0
γ	90.0
V	32367(5) $Å^3$
F (000)	16592
μMoK_a	2.85
λMoK_a	0.71073
D_{calc}	1.580 Mg m^{-3}
Z	16
Independent Refl.	2787
Obs. Refl. ($F>4.0\sigma(F)$)	1075
R/R_w	8.74/7.81%
Space Group	I-43d
Octants Meas.	$-1 \leq h \leq 20$, $-1 \leq k \leq 37$, $-1 \leq l \leq 37$

TABLE XXII

POSITIONAL PARAMETERS FOR
$[CuIP(C_6H_4Me\text{-}m)_3]_4$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I(1)	9123(1)	3823(1)	166(1)
Cu(2)	9088(2)	4676(2)	88(2)
P(2)	8711(4)	4926(4)	-445(4)
C(40)	8136(20)	4735(14)	-483(18)
C(41)	8109(14)	4306(14)	-482(11)
C(42)	7745(16)	4121(20)	-506(14)
C(43)	7428(19)	4350(26)	-550(22)
C(44)	7383(24)	4765(30)	-531(17)
C(45)	7788(21)	4959(24)	-522(19)
C(46)	7682(17)	3615(12)	-518(16)
C(10)	8478(14)	3087(17)	1116(21)
C(11)	8425(19)	2734(26)	1400(19)
C(12)	8378(16)	2341(18)	1212(26)
C(13)	8215(14)	2306(21)	876(25)
C(14)	8296(16)	2631(19)	588(22)
C(15)	8386(14)	2986(20)	750(14)
C(16)	8232(19)	2636(15)	110(16)
C(20)	8676(13)	5525(14)	-445(18)
C(21)	8658(19)	5800(25)	-797(14)
C(22)	8669(17)	6233(20)	-836(26)
C(23)	8504(20)	6387(14)	-333(23)
C(24)	8505(17)	6150(15)	-21(20)
C(25)	8575(15)	5755(26)	-127(22)
C(26)	8644(27)	6493(20)	-1143(16)
C(30)	9610(11)	4661(12)	-1298(10)
C(31)	9356	4777	-960
C(32)	8926	4834	-1018
C(33)	8749	4774	-1414
C(34)	9002	4657	-1752
C(35)	9432	4601	-1693
Cu(1A)	6002(2)	6002(2)	6002(2)
P(1A)	6402(4)	6402(4)	6402(4)
I(2A)	5094(1)	5094(1)	5094(1)

TABLE XXIII

HYDROGEN POSITIONAL PARAMETERS FOR
[CuIP(C_6H_4Me-*m*)$_3$]$_4$

ATOM	x	y	z
H(41A)	8356	4137	-455
H(43A)	7158	4219	-577
H(44A)	7136	4934	-558
H(45A)	7810	5259	-522
H(46A)	7391	3542	-547
H(46B)	7838	3501	-749
H(46C)	7788	3502	-260
H(10A)	8551	3357	1229
H(11A)	8475	2765	1695
H(12A)	8355	2103	1395
H(13A)	8142	2036	764
H(15A)	8409	3224	567
H(16A)	8159	2364	4
H(16B)	8021	2835	29
H(16C)	8498	2720	-3
H(21A)	8719	5675	-1064
H(23A)	8474	6686	-310
H(24A)	8444	6276	246
H(25A)	8545	5581	118
H(26A)	8706	6329	-1388
H(26B)	8381	6635	-1181
H(26C)	8862	6696	-1100

TABLE XXIV

ANISOTROPIC THERMAL PARAMETERS FOR
$[CuIP(C_6H_4Me\text{-}m)_3]_4$

ATOM	U11	U22	U33	U12	U13	U23
I(1)	52(2)	52(2)	53(2)	0(2)	-5(2)	-10(2)
Cu(2)	70(5)	80(5)	69(5)	-1(4)	-12(5)	-3(5)
P(2)	36(9)	34(9)	68(11)	-4(8)	-12(8)	8(8)
C(40)	130(62)	0(29)	104(51)	-14(36)	98(46)	17(32)
C(41)	40(39)	59(42)	0(26)	-78(33)	38(25)	21(26)
C(42)	13(33)	141(57)	19(33)	-10(40)	50(29)	16(35)
C(43)	0(40)	159(103)	166(76)	-55(53)	71(44)	-79(74)
C(44)	103(64)	336(132)	30(39)	181(81)	-104(44)	-9(58)
C(45)	133(66)	212(80)	114(60)	162(68)	-29(53)	120(56)
C(46)	197(69)	46(34)	154(61)	-182(43)	27(51)	-14(37)
C(10)	10(29)	69(46)	157(58)	-28(29)	-115(36)	16(42)
C(11)	99(53)	245(90)	56(41)	-28(61)	9(41)	-166(55
C(12)	41(42)	33(42)	312(116	-10(35)	-81(55)	-97(59)
C(13)	0(30)	129(55)	255(92)	-129(35)	29(43)	-24(58)
C(14)	45(40)	128(50)	181(77)	-122(39)	-24(45)	-179(56
C(15)	0(26)	205(70)	8(27)	14(35)	-31(25)	19(38)
C(16)	170(72)	105(49)	143(56)	-56(50)	-4(53)	-173(48
C(20)	4(28)	27(30)	130(50)	25(25)	11(32)	-22(33)
C(21)	170(66)	245(95)	0(30)	-228(71)	-50(37)	35(45)
C(22)	44(38)	77(42)	127(89)	-60(36)	-20(48)	-4(56)
C(23)	246(94)	9(29)	300(99)	109(45)	-306(91)	12(45)
C(24)	221(78)	134(51)	176(64)	235(58)	-236(64)	-131(53
C(25)	69(44)	511(122)	355(98)	175(59)	79(49)	-381(98
C(26)	592(185)	233(100)	113(66)	-233(111	-190(93)	248(78)
C(30)	1761(333)	26(53)	113(40)	18(109	-627(112	43(44)
C(31)	259(69)	0(28)	20(30)	-30(36)	-104(41)	44(27)
C(32)	3568(725)	54(45)	2353(495)	-424(152	-3023(597)	309(12
C(33)	47(35)	0(32)	350(115)	13(29)	1(60)	-17(59)
C(34)	423(178)	21(48)	0(32)	-19(76)	44(64)	-26(30)
C(35)	1000(615)	0(56)	534(170)	-132(166)	605(253)	-34(92)
Cu(1A)	61(4)	61(4)	61(4)	-11(4)	-11(4)	-11(4)
P(1A)	42(7)	42(7)	42(7)	11(8)	11(8)	11(8)
I(2A)	56(2)	56(2)	56(2)	5(2)	5(2)	5(2)

The anisotropic displacement exponent takes the form:

$$-2p^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE XXV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
$[CuIP(C_6H_4Me\text{-}m)_3]_4$

I(1)-Cu(2)	2.731 (7)	Cu(2)-I(1)-Cu(2C)	75.1(3)
I(1)-Cu(2C)	2.699 (8)	Cu(2)-I(1)-Cu(1B)	83.1(2)
I(1)-Cu(1B)	2.754 (6)	Cu(2C)-I(1)-Cu(1B)	83.7(2)
I(2A)-Cu(2A)	2.706 (8)	I(1)-Cu(2)-P(2)	116.5(4)
I(2A)-Cu(2B)	2.706 (8)	I(1)-Cu(2)-I(1D)	96.6(3)
I(2A)-Cu(2D)	2.706 (8)	P(2)-Cu(2)-I(1D)	118.3(5)
Cu(2)-P(2)	2.229 (15)	I(1)-Cu(2)-I(2AA)	103.3(2)
Cu(2)-I(1D)	2.699 (8)	P(2)-Cu(2)-I(2AA)	115.4(4)
Cu(2)-I(2AA)	2.706 (8)	I(1D)-Cu(2)-I(2AA)	104.1(2)
Cu(1A)-P(1A)	2.205 (26)	P(1A)-Cu(1A)-I(1A)	121.8(2)
Cu(1A)-I(1A)	2.754 (6)	P(1A)-Cu(1A)-I(1B)	121.8(2)
Cu(1A)-I(1B)	2.754 (6)	I(1A)-Cu(1A)-I(1B)	94.8(3)
Cu(1A)-I(1C)	2.754 (6)	P(1A)-Cu(1A)-I(1C)	121.8(2)
P(2)-C(40)	1.934 (64)	I(1A)-Cu(1A)-I(1C)	94.8(3)
P(2)-C(20)	1.911 (45)	I(1B)-Cu(1A)-I(1C)	94.8(3)
P(2)-C(32)	1.973 (34)	Cu(1A)-P(1A)-C(10A)	109.5(19)
P(1A)-C(10A)	1.904 (59)	Cu(1A)-P(1A)-C(10B)	109.5(19)
P(1A)-C(10B)	1.904 (59)	C(10A)-P(1A)-C(10B)	109.5(19)
P(1A)-C(10C)	1.904 (59)	Cu(1A)-P(1A)-C(10C)	109.5(19)
C(40)-C(41)	1.370 (64)	C(10A)-P(1A)-C(10C)	109.5(19)
C(40)-C(45)	1.325 (91)	C(10B)-P(1A)-C(10C)	109.5(19)
C(41)-C(42)	1.304 (71)	Cu(2A)-I(2A)-Cu(2B)	75.4(3)
C(42)-C(43)	1.255 (88)	Cu(2A)-I(2A)-Cu(2D)	75.4(3)
C(42)-C(46)	1.623 (74)	Cu(2B)-I(2A)-Cu(2D)	75.4(3)
C(43)-C(44)	1.330 (124)	Cu(2)-P(2)-C(40)	116.5(18)
C(44)-C(45)	1.430 (106)	Cu(2)-P(2)-C(20)	112.9(17)
C(10)-C(11)	1.453 (96)	C(40)-P(2)-C(20)	105.0(20)
C(10)-C(15)	1.247 (79)	Cu(2)-P(2)-C(32)	117.7(12)
C(10)-P(1AA)	1.904 (59)	C(40)-P(2)-C(32)	103.0(21)
C(11)-C(12)	1.395 (101)	C(20)-P(2)-C(32)	99.7(21)
C(12)-C(13)	1.196 (106)	P(2)-C(40)-C(41)	112.1(40)
C(13)-C(14)	1.409 (96)	P(2)-C(40)-C(45)	129.0(45)
C(14)-C(15)	1.275 (86)	C(41)-C(40)-C(45)	118.9(58)
C(14)-C(16)	1.536 (86)	C(40)-C(41)-C(42)	120.7(51)
C(20)-C(21)	1.425 (79)	C(41)-C(42)-C(43)	117.2(62)
C(20)-C(25)	1.293 (89)	C(41)-C(42)-C(46)	124.1(48)
C(21)-C(22)	1.384 (103)	C(43)-C(42)-C(46)	118.5(55)
C(22)-C(23)	1.758 (106)	C(42)-C(43)-C(44)	131.3(69)
C(22)-C(26)	1.284 (94)	C(43)-C(44)-C(45)	109.5(67)
C(23)-C(24)	1.247 (87)	C(40)-C(45)-C(44)	121.6(71)
C(24)-C(25)	1.324 (95)	C(11)-C(10)-C(15)	110.7(55)
		C(11)-C(10)-P(1AA)	112.9(47)

Table XXV (Continued)

	C(15)-C(10)-P(1AA)	135.8(51)
	C(10)-C(11)-C(12)	116.2(58)
	C(11)-C(12)-C(13)	120.9(63)
	C(12)-C(13)-C(14)	115.8(59)
	C(13)-C(14)-C(15)	115.4(62)
	C(13)-C(14)-C(16)	129.1(55)
	C(15)-C(14)-C(16)	114.9(52)
	C(10)-C(15)-C(14)	131.5(62)
	P(2)-C(20)-C(21)	128.2(45)
	P(2)-C(20)-C(25)	125.4(50)
	C(21)-C(20)-C(25)	104.9(53)
	C(20)-C(21)-C(22)	133.2(57)
	C(21)-C(22)-C(23)	100.8(50)
	C(21)-C(22)-C(26)	135.2(71)
	C(23)-C(22)-C(26)	119.7(54)
	C(22)-C(23)-C(24)	123.8(47)
	C(23)-C(24)-C(25)	112.1(61)
	C(20)-C(25)-C(24)	141.3(71)
	P(2)-C(32)-C(31)	103.8(11)
	P(2)-C(32)-C(33)	135.8(11)

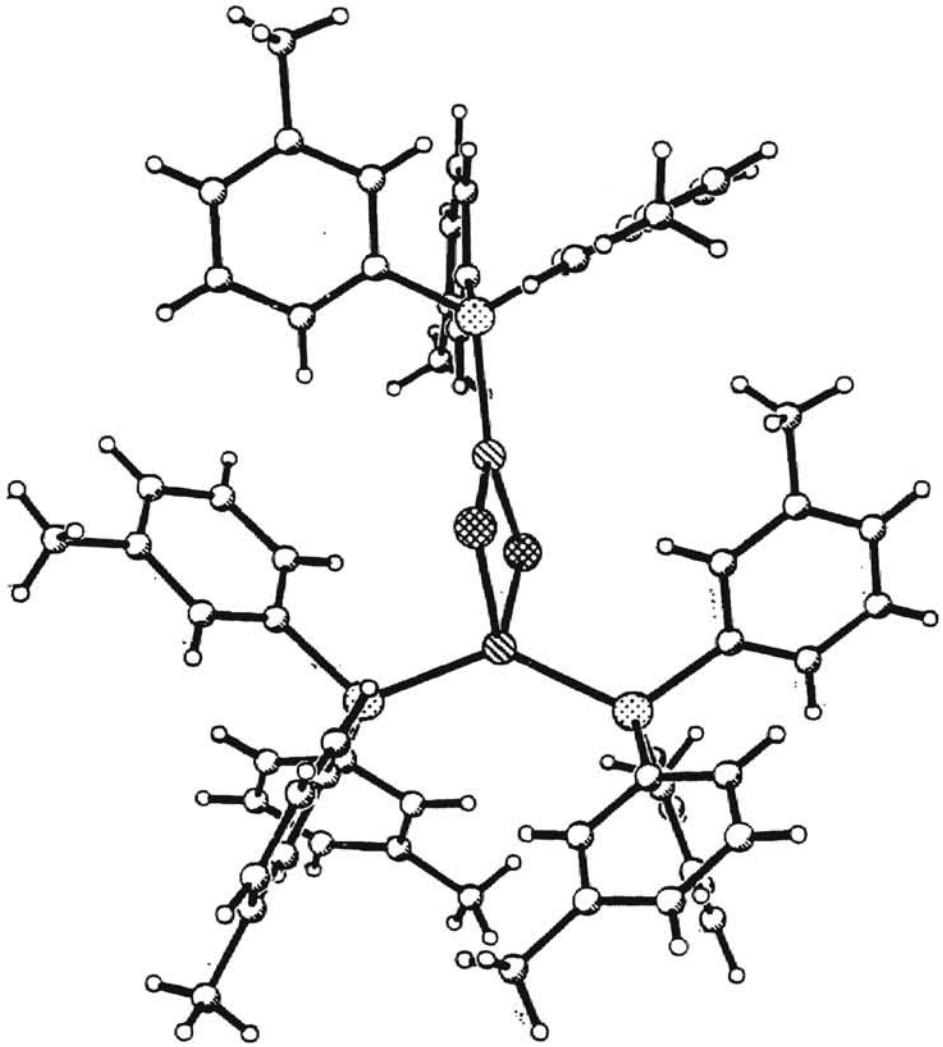


Figure 14. Projection view of $Cu_2Br_2(P(C_6H_4Me\text{-}m)_3)_3$

TABLE XXVI

CRYSTAL DATA FOR $Cu_2Br_2(P(C_6H_4Me\text{-}m)_3)_3$

Formula	$CuBrPC_{21}H_{21}$
MWT	447.80
a	11.552(2) Å
b	13.633(2)
c	19.160(3)
α	86.460(10)°
β	86.840(10)
γ	73.160(10)
V	2880.4(8) $Å^3$
F (000)	1356
μMoK_a	3.301cm^{-1}
λMoK_a	0.71073 Å
D_{calc}	1.549 Mg m^{-3}
Z	6
Independent Refl.	11262
Obs. Refl. ($F>4.0\sigma(F)$)	3111
R/R_w	11.7/13.4%
Space Group	P_1
Octants Meas.	$-1 \le h \le 10, -17 \le k \le 17$
	$-24 \le l \le 24$

TABLE XXVII

POSITIONAL PARAMETERS FOR
$Cu_2Br_2(P(C_6H_4Me\text{-}m)_3)_3$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br1	0.7884(2)	0.88240(13)	0.33764(9)
Br2	1.0298(2)	0.92939(13)	0.19401(9)
Cu2	0.9794(2)	0.81136(15)	0.27908(11)
Cu1	0.8122(2)	1.01956(14)	0.24101(10)
P2	0.7035(4)	1.0101(3)	0.1487(2)
P1	1.1116(4)	0.6603(3)	0.2972(2)
P3	0.8174(4)	1.1520(3)	0.3041(2)
C30	0.6726(14)	1.2224(12)	0.3470(8)
C31	0.6244(16)	1.3293(12)	0.3393(8)
C32	0.5150(18)	1.3738(13)	0.3753(9)
C33	0.4563(16)	1.3149(13)	0.4158(9)
C34	0.5015(16)	1.2101(14)	0.4242(8)
C35	0.6119(15)	1.1654(10)	0.3883(8)
C36	0.4379(16)	1.1470(14)	0.4697(9)
C310	0.8601(15)	1.2544(11)	0.2520(8)
C311	0.9405(15)	1.3009(12)	0.2724(8)
C312	0.9658(15)	1.3829(13)	0.2298(10)
C313	0.9043(18)	1.4174(13)	0.1711(10)
C314	0.8205(17)	1.3694(12)	0.1498(9)
C315	0.8041(17)	1.2871(12)	0.1893(9)
C316	0.7586(18)	1.4075(13)	0.0829(8)
C210	0.5379(15)	1.0317(11)	0.1656(8)
C211	0.4733(16)	0.9865(14)	0.1301(10)
C212	0.3562(21)	1.0003(16)	0.1433(11)
C213	0.2967(18)	1.0675(15)	0.1936(11)
C214	0.3573(18)	1.1197(15)	0.2297(10)
C215	0.4818(15)	1.1002(12)	0.2172(8)
C110	1.2478(13)	0.6702(11)	0.3383(9)
C111	1.2638(15)	0.6440(11)	0.4097(9)
C112	1.3636(18)	0.6610(13)	0.4385(10)
C113	1.4458(16)	0.6970(14)	0.4010(10)
C114	1.4262(17)	0.7245(14)	0.3303(11)
C115	1.3286(16)	0.7127(14)	0.3003(9)
C116	1.5096(18)	0.7696(16)	0.2870(10)
C10	1.0584(16)	0.5661(12)	0.3509(8)
C11	1.1378(15)	0.4687(13)	0.3711(8)
C12	1.0937(17)	0.3978(12)	0.4115(8)
C13	0.9692(19)	0.4248(13)	0.4282(8)
C14	0.8890(17)	0.5163(14)	0.4063(9)
C15	0.9383(14)	0.5865(12)	0.3685(8)
C16	0.7574(16)	0.5396(14)	0.4245(10)
C220	0.7123(16)	1.0996(12)	0.0727(8)

Table XXVII (continued)

C221	0.8288(17)	1.0984(13)	0.0504(9)
C222	0.8454(18)	1.1551(15)	-0.0094(10)
C223	0.7495(21)	1.2119(14)	-0.0470(9)
C224	0.6317(20)	1.2165(13)	-0.0216(9)
C225	0.6137(17)	1.1578(13)	0.0356(9)
C226	0.5220(19)	1.2805(13)	-0.0609(9)
C20	0.7492(13)	0.8844(10)	0.1112(8)
C21	0.7470(15)	0.8010(12)	0.1565(9)
C22	0.7797(16)	0.7043(12)	0.1305(10)
C23	0.8183(15)	0.6860(14)	0.0636(10)
C24	0.8235(17)	0.7671(17)	0.0185(9)
C25	0.7864(15)	0.8686(12)	0.0423(8)
C26	0.8661(18)	0.7521(13)	-0.0551(9)
C120	1.1733(15)	0.5910(11)	0.2174(8)
C121	1.1006(16)	0.6109(13)	0.1613(10)
C122	1.1443(18)	0.5551(16)	0.1008(10)
C123	1.2524(18)	0.4819(14)	0.1001(10)
C124	1.3224(21)	0.4630(14)	0.1569(11)
C125	1.2844(17)	0.5164(12)	0.2168(9)
C126	1.4438(21)	0.3826(16)	0.1539(10)
C320	0.9210(14)	1.1264(11)	0.3764(7)
C321	0.8970(16)	1.1709(11)	0.4393(9)
C322	0.9827(20)	1.1494(12)	0.4890(8)
C323	1.0942(17)	1.0821(12)	0.4764(9)
C324	1.1225(17)	1.0371(13)	0.4151(10)
C325	1.0328(16)	1.0560(12)	0.3654(8)
C326	1.2427(16)	0.9598(13)	0.4024(9)
C216	0.2972(15)	1.1995(14)	0.2838(8)

TABLE XXVIII

HYDROGEN POSITIONAL PARAMETERS FOR
$Cu_2Br_2(P(C_6H_4Me\text{-}m)_3)_3$

ATOM	x	y	z
H31A	0.6649(16)	1.3703(12)	0.3105(8)
H32A	0.4800(18)	1.4469(13)	0.3727(9)
H33A	0.3798(16)	1.3470(13)	0.4387(9)
H35A	0.6457(15)	1.0923(10)	0.3926(8)
H36A	0.3648(16)	1.1909(14)	0.4900(9)
H36B	0.4184(16)	1.0980(14)	0.4420(9)
H36C	0.4898(16)	1.1115(14)	0.5063(9)
H31C	0.9803(15)	1.2783(12)	0.3157(8)
H31D	1.0252(15)	1.4141(13)	0.2434(10)
H31E	0.9198(18)	1.4738(13)	0.1434(10)
H31F	0.7502(17)	1.2517(12)	0.1738(9)
H31G	0.7037(18)	1.3686(13)	0.0750(8)
H31H	0.7143(18)	1.4786(13)	0.0862(8)
H31I	0.8173(18)	1.4001(13)	0.0446(8)
H21A	0.5141(16)	0.9433(14)	0.0933(10)
H21B	0.3134(21)	0.9637(16)	0.1183(11)
H21C	0.2121(18)	1.0772(15)	0.2042(11)
H21D	0.5283(15)	1.1322(12)	0.2433(8)
H11A	1.2081(15)	0.6154(11)	0.4369(9)
H11C	1.3744(18)	0.6469(13)	0.4878(10)
H11D	1.5167(16)	0.7036(14)	0.4218(10)
H11E	1.3146(16)	0.7336(14)	0.2520(9)
H11F	1.4812(18)	0.7828(16)	0.2402(10)
H11G	1.5103(18)	0.8329(16)	0.3060(10)
H11H	1.5900(18)	0.7233(16)	0.2862(10)
H11I	1.2221(15)	0.4513(13)	0.3573(8)
H12A	1.1455(17)	0.3325(12)	0.4273(8)
H13A	0.9367(19)	0.3770(13)	0.4557(8)
H15A	0.8861(14)	0.6524(12)	0.3540(8)
H16A	0.7414(16)	0.4823(14)	0.4507(10)
H16B	0.7323(16)	0.5992(14)	0.4520(10)
H16C	0.7133(16)	0.5525(14)	0.3822(10)
H22A	0.8959(17)	1.0599(13)	0.0775(9)
H22B	0.9257(18)	1.1547(15)	-0.0256(10)
H22C	0.7613(21)	1.2480(14)	-0.0902(9)
H22D	0.5334(17)	1.1570(13)	0.0508(9)
H22H	0.4686(19)	1.3274(13)	-0.0298(9)
H22F	0.5457(19)	1.3183(13)	-0.1003(9)
H22G	0.4810(19)	1.2346(13)	-0.0768(9)
H21E	0.7226(15)	0.8118(12)	0.2048(9)
H22I	0.7766(16)	0.6470(12)	0.1615(10)
H23A	0.8410(15)	0.6177(14)	0.0471(10)

Table XXVIII(continued)

H25A	0.7868(15)	0.9258(12)	0.0105(8)
H26A	0.8887(18)	0.6806(13)	-0.0647(9)
H26B	0.8028(18)	0.7894(13)	-0.0852(9)
H26C	0.9351(18)	0.7777(13)	-0.0632(9)
H12B	1.0217(16)	0.6596(13)	0.1634(10)
H12D	1.0978(18)	0.5683(16)	0.0594(10)
H12E	1.2805(18)	0.4435(14)	0.0591(10)
H12F	1.3324(17)	0.5021(12)	0.2575(9)
H12G	1.4836(21)	0.3774(16)	0.1973(10)
H12H	1.4304(21)	0.3180(16)	0.1459(10)
H12I	1.4938(21)	0.4000(16)	0.1163(10)
H32B	0.8193(16)	1.2189(11)	0.4485(9)
H32C	0.9643(20)	1.1808(12)	0.5333(8)
H32D	1.1540(17)	1.0676(12)	0.5114(9)
H32E	1.0507(16)	1.0214(12)	0.3223(8)
H32F	1.2930(16)	0.9547(13)	0.4415(9)
H32G	1.2302(16)	0.8943(13)	0.3963(9)
H32H	1.2816(16)	0.9806(13)	0.3609(9)
H21F	0.2119(15)	1.2070(14)	0.2883(8)
H21G	0.3330(15)	1.1770(14)	0.3282(8)
H21H	0.3099(15)	1.2643(14)	0.2689(8)

TABLE XXIX

ANISOTROPIC THERMAL PARAMETERS FOR
$Cu_2Br_2(P(C_6H_4Me\text{-}m)_3)_3$

ATOM	U11	U22	U33	U12	U13	U23
Br1	0.0520(15)	0.0394(11)	0.0492(13)	0.0008(9)	0.0038(11)	-0.0087(10)
Br2	0.0398(13)	0.0498(12)	0.0486(12)	-0.0015(10)	0.0059(10)	-0.0074(10)
Cu2	0.046(2)	0.0372(14)	0.062(2)	0.0005(12)	-0.0069(13)	-0.0056(12)
Cu1	0.041(2)	0.0359(13)	0.0449(14)	-0.0061(11)	-0.0063(12)	-0.0050(12)
P2	0.036(3)	0.030(3)	0.041(3)	-0.005(2)	-0.002(2)	-0.012(2)
P1	0.037(3)	0.035(3)	0.044(3)	-0.003(2)	0.001(3)	-0.009(2)
P3	0.041(3)	0.028(2)	0.032(3)	-0.004(2)	-0.007(2)	-0.007(2)
C30	0.020(11)	0.040(11)	0.036(11)	-0.010(9)	-0.001(9)	-0.003(9)
C31	0.057(14)	0.038(11)	0.038(11)	-0.017(9)	0.011(10)	-0.008(10)
C32	0.072(17)	0.038(12)	0.049(13)	-0.010(10)	-0.011(12)	-0.011(12)
C33	0.038(14)	0.038(12)	0.065(14)	-0.010(10)	-0.017(11)	0.028(10)
C34	0.036(13)	0.070(14)	0.032(11)	-0.008(10)	-0.003(10)	-0.013(11)
C35	0.044(13)	0.011(9)	0.042(11)	-0.016(8)	-0.008(10)	0.016(9)
C36	0.069(17)	0.107(18)	0.061(14)	-0.014(13)	0.030(13)	-0.024(14)
C310	0.049(13)	0.023(9)	0.027(10)	-0.018(8)	-0.002(9)	-0.010(9)
C311	0.052(14)	0.048(12)	0.045(12)	-0.018(10)	0.011(10)	-0.023(11)
C312	0.035(14)	0.042(12)	0.089(17)	-0.006(11)	0.000(12)	-0.009(11)
C313	0.078(17)	0.036(12)	0.062(14)	0.014(10)	0.012(13)	-0.025(12)
C314	0.075(16)	0.026(10)	0.039(12)	-0.010(9)	0.017(11)	-0.023(11)
C315	0.078(16)	0.043(12)	0.044(12)	-0.013(10)	-0.003(12)	-0.027(11)
C316	0.143(22)	0.102(17)	0.044(13)	0.048(12)	-0.031(14)	-0.076(16)
C210	0.035(12)	0.024(10)	0.045(12)	0.003(8)	-0.020(10)	0.002(9)
C211	0.012(13)	0.082(16)	0.074(15)	-0.020(12)	0.004(11)	-0.008(11)
C212	0.076(20)	0.100(19)	0.078(17)	-0.021(14)	-0.046(15)	-0.047(16)
C213	0.042(16)	0.076(17)	0.082(18)	0.015(13)	-0.005(14)	-0.011(13)
C214	0.035(15)	0.086(17)	0.061(15)	-0.032(12)	-0.006(12)	0.008(13)
C215	0.015(12)	0.042(11)	0.053(12)	-0.001(9)	-0.004(9)	0.002(9)
C110	0.005(10)	0.035(10)	0.043(11)	-0.004(8)	0.009(9)	0.016(8)
C111	0.040(14)	0.032(10)	0.052(13)	-0.003(9)	0.009(10)	-0.010(9)
C112	0.053(16)	0.081(16)	0.062(15)	-0.024(12)	-0.019(13)	-0.031(13)
C113	0.016(13)	0.094(16)	0.062(15)	-0.016(12)	0.007(11)	-0.026(12)
C114	0.020(14)	0.060(13)	0.066(16)	-0.005(11)	0.028(12)	-0.012(11)
C115	0.020(14)	0.113(18)	0.048(13)	0.001(12)	0.008(11)	-0.015(13)
C116	0.073(20)	0.182(26)	0.112(21)	-0.027(19)	-0.021(17)	-0.059(19)
C10	0.041(13)	0.041(11)	0.030(10)	-0.015(9)	0.003(9)	-0.017(10)
C11	0.035(13)	0.059(13)	0.038(11)	-0.007(10)	0.002(9)	-0.015(11)
C12	0.046(14)	0.042(12)	0.046(12)	0.008(9)	0.006(11)	0.001(11)
C13	0.087(18)	0.045(13)	0.040(12)	0.004(10)	0.004(12)	-0.035(13)
C14	0.050(14)	0.049(12)	0.045(12)	0.021(10)	-0.007(11)	-0.025(11)
C15	0.016(12)	0.033(10)	0.058(12)	0.000(9)	0.005(9)	0.000(9)
C16	0.058(18)	0.104(19)	0.123(20)	0.004(15)	0.017(15)	-0.039(15)
C220	0.021(11)	0.051(11)	0.039(11)	-0.029(9)	0.035(9)	-0.030(10)
C221	0.059(16)	0.060(13)	0.053(13)	0.007(10)	-0.001(12)	-0.036(12)
C222	0.050(16)	0.090(17)	0.064(15)	-0.019(13)	-0.017(13)	-0.036(14)
C223	0.090(19)	0.065(15)	0.043(13)	0.000(11)	0.015(14)	-0.061(14)
C224	0.084(18)	0.041(12)	0.029(11)	0.000(9)	-0.008(12)	-0.020(12)

Table XXIX (continued)

C225	0.049(15)	0.061(13)	0.046(13)	-0.018(11)	-0.013(11)	-0.013(12)
C226	0.145(24)	0.078(16)	0.083(17)	0.027(13)	-0.050(17)	-0.015(16)
C20	0.015(10)	0.015(8)	0.041(10)	-0.017(8)	0.006(8)	0.008(7)
C21	0.051(14)	0.035(11)	0.071(14)	-0.001(10)	-0.015(11)	-0.019(10)
C22	0.054(14)	0.033(11)	0.079(15)	-0.020(10)	-0.004(12)	-0.017(10)
C23	0.046(14)	0.060(13)	0.055(13)	-0.044(11)	0.007(11)	-0.020(11)
C24	0.051(15)	0.106(19)	0.034(12)	-0.001(13)	0.008(11)	-0.034(14)
C25	0.065(14)	0.033(11)	0.029(10)	-0.018(8)	0.002(10)	-0.011(10)
C26	0.121(21)	0.063(14)	0.079(17)	-0.025(13)	0.005(16)	0.003(14)
C120	0.044(13)	0.021(9)	0.044(11)	-0.007(8)	-0.030(10)	-0.012(9)
C121	0.040(14)	0.068(14)	0.058(14)	0.028(11)	0.003(12)	-0.007(11)
C122	0.052(16)	0.120(20)	0.045(14)	0.008(13)	0.003(12)	-0.030(15)
C123	0.051(16)	0.067(15)	0.069(16)	-0.016(12)	-0.017(13)	-0.002(12)
C124	0.091(20)	0.043(13)	0.074(17)	0.012(12)	-0.026(16)	0.012(13)
C125	0.074(16)	0.032(11)	0.050(13)	-0.012(10)	-0.013(12)	-0.002(11)
C126	0.166(30)	0.142(24)	0.094(20)	-0.032(18)	-0.027(20)	0.022(23)
C320	0.036(12)	0.024(9)	0.031(10)	-0.009(8)	0.004(9)	-0.018(9)
C321	0.050(14)	0.034(10)	0.053(13)	-0.023(9)	-0.006(11)	0.003(10)
C322	0.124(21)	0.038(12)	0.025(11)	-0.014(9)	-0.028(13)	-0.016(13)
C323	0.056(15)	0.036(11)	0.044(12)	0.002(9)	-0.022(11)	-0.001(10)
C324	0.040(14)	0.042(12)	0.063(14)	-0.013(11)	-0.006(12)	-0.005(10)
C325	0.053(14)	0.047(12)	0.027(10)	-0.007(9)	0.005(10)	-0.017(11)
C326	0.068(17)	0.091(16)	0.098(18)	-0.010(14)	-0.035(14)	-0.027(14)
C216	0.032(14)	0.155(21)	0.071(15)	-0.042(15)	0.008(12)	-0.018(14)

The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

TABLE XXX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $Cu_2Br_2(P(C_6H_4Me\text{-}m)_3)_3$

Br1 Cu2	2.386(3)	Cu2 Br1 Cu1	73.86(9)
Br1 Cu1	2.611(3)	Cu2 Br2 Cu1	74.11(9)
Br2 Cu2	2.387(3)	P1 Cu2 Br1	128.9(2)
Br2 Cu1	2.596(3)	P1 Cu2 Br2	118.6(2)
Cu2 P1	2.201(5)	Br1 Cu2 Br2	112.42(10)
Cu2 Cu1	3.007(3)	P1 Cu2 Cu1	174.4(2)
Cu1 P3	2.251(4)	Br1 Cu2 Cu1	56.50(7)
Cu1 P2	2.256(5)	Br2 Cu2 Cu1	56.11(7)
P2 C20	1.821(13)	P3 Cu1 P2	132.1(2)
P2 C210	1.86(2)	P3 Cu1 Br2	108.9(2)
P2 C220	1.86(2)	P2 Cu1 Br2	100.74(14)
P1 C10	1.82(2)	P3 Cu1 Br1	102.55(14)
P1 C110	1.84(2)	P2 Cu1 Br1	108.92(14)
P1 C120	1.85(2)	Br2 Cu1 Br1	99.26(9)
P3 C320	1.830(15)	P3 Cu1 Cu2	117.88(14)
P3 C310	1.83(2)	P2 Cu1 Cu2	110.01(13)
P3 C30	1.846(15)	Br2 Cu1 Cu2	49.77(7)
C30 C35	1.38(2)	Br1 Cu1 Cu2	49.64(7)
C30 C31	1.40(2)	C20 P2 C210	102.2(7)
C31 C32	1.40(2)	C20 P2 C220	103.7(7)
C32 C33	1.37(2)	C210 P2 C220	103.7(7)
C33 C34	1.37(2)	C20 P2 Cu1	113.3(5)
C34 C35	1.41(2)	C210 P2 Cu1	116.6(6)
C34 C36	1.50(2)	C220 P2 Cu1	115.6(5)
C310 C311	1.35(2)	C10 P1 C110	106.1(8)
C310 C315	1.38(2)	C10 P1 C120	102.8(7)
C311 C312	1.43(2)	C110 P1 C120	103.2(7)
C312 C313	1.35(2)	C10 P1 Cu2	116.4(6)
C313 C314	1.41(2)	C110 P1 Cu2	112.0(5)
C314 C315	1.37(2)	C120 P1 Cu2	115.0(5)
C314 C316	1.49(2)	C320 P3 C310	102.6(7)
C210 C211	1.33(2)	C320 P3 C30	102.1(7)
C210 C215	1.40(2)	C310 P3 C30	102.3(7)
C211 C212	1.32(2)	C320 P3 Cu1	118.2(5)
C212 C213	1.38(2)	C310 P3 Cu1	113.5(5)
C213 C214	1.37(2)	C30 P3 Cu1	116.0(5)
C214 C215	1.39(2)	C35 C30 C31	120.0(15)
C214 C216	1.54(2)	C35 C30 P3	117.2(12)
C110 C115	1.39(2)	C31 C30 P3	122.8(14)
C110 C111	1.40(2)	C32 C31 C30	117.4(16)
C111 C112	1.39(2)	C33 C32 C31	121.2(17)
C112 C113	1.35(2)	C34 C33 C32	122.6(18)
C113 C114	1.40(2)	C33 C34 C35	116.2(17)
C114 C115	1.35(2)	C33 C34 C36	122.1(18)
C114 C116	1.48(2)	C35 C34 C36	121.7(17)
C10 C15	1.36(2)	C30 C35 C34	122.6(14)
C10 C11	1.42(2)	C311 C310 C315	118.7(16)
C11 C12	1.39(2)	C311 C310 P3	123.7(13)

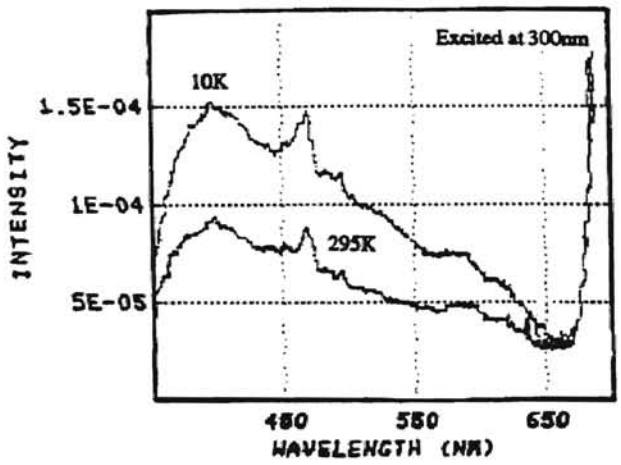
Table XXX (continued)

C12 C13	1.40(2)	C315 C310 P3	117.6(13)
C13 C14	1.38(2)	C310 C311 C312	120.3(17)
C14 C15	1.40(2)	C313 C312 C311	119.7(18)
C14 C16	1.49(2)	C312 C313 C314	120.1(17)
C220 C221	1.39(2)	C315 C314 C313	118.6(18)
C220 C225	1.39(2)	C315 C314 C316	123.2(18)
C221 C222	1.38(2)	C313 C314 C316	118.1(16)
C222 C223	1.37(2)	C314 C315 C310	122.3(18)
C223 C224	1.40(2)	C211 C210 C215	120.4(17)
C224 C225	1.36(2)	C211 C210 P2	122.6(14)
C224 C226	1.52(2)	C215 C210 P2	117.0(13)
C20 C25	1.37(2)	C212 C211 C210	122.4(19)
C20 C21	1.39(2)	C211 C212 C213	119.2(19)
C21 C22	1.38(2)	C214 C213 C212	121.0(20)
C22 C23	1.35(2)	C213 C214 C215	118.7(18)
C23 C24	1.37(2)	C213 C214 C216	124.3(19)
C24 C25	1.42(2)	C215 C214 C216	117.0(18)
C24 C26	1.47(2)	C210 C215 C214	118.2(17)
C120 C121	1.37(2)	C115 C110 C111	119.8(16)
C120 C125	1.39(2)	C115 C110 P1	120.0(13)
C121 C122	1.41(2)	C111 C110 P1	119.9(14)
C122 C123	1.35(2)	C112 C111 C110	116.9(16)
C123 C124	1.36(2)	C113 C112 C111	123.5(18)
C124 C125	1.38(2)	C112 C113 C114	118.4(18)
C124 C126	1.51(2)	C115 C114 C113	120.5(18)
C320 C321	1.36(2)	C115 C114 C116	118.3(19)
C320 C325	1.38(2)	C113 C114 C116	121.2(20)
C321 C322	1.37(2)	C114 C115 C110	120.9(17)
C322 C323	1.37(2)	C15 C10 C11	118.9(16)
C323 C324	1.34(2)	C15 C10 P1	119.3(13)
C324 C325	1.40(2)	C11 C10 P1	121.7(14)
C324 C326	1.50(2)	C12 C11 C10	120.2(16)
		C11 C12 C13	117.5(16)
		C14 C13 C12	123.7(18)
		C13 C14 C15	116.6(18)
		C13 C14 C16	121.2(17)
		C15 C14 C16	122.1(17)
		C10 C15 C14	122.9(16)
		C221 C220 C225	120.3(17)
		C221 C220 P2	114.7(15)
		C225 C220 P2	124.8(13)
		C220 C221 C222	119.1(18)
		C221 C222 C223	121.3(19)
		C222 C223 C224	118.8(18)
		C225 C224 C223	120.6(19)
		C225 C224 C226	118.5(20)
		C223 C224 C226	120.7(18)
		C224 C225 C220	119.6(19)
		C25 C20 C21	119.7(14)
		C25 C20 P2	123.8(12)
		C21 C20 P2	116.5(12)

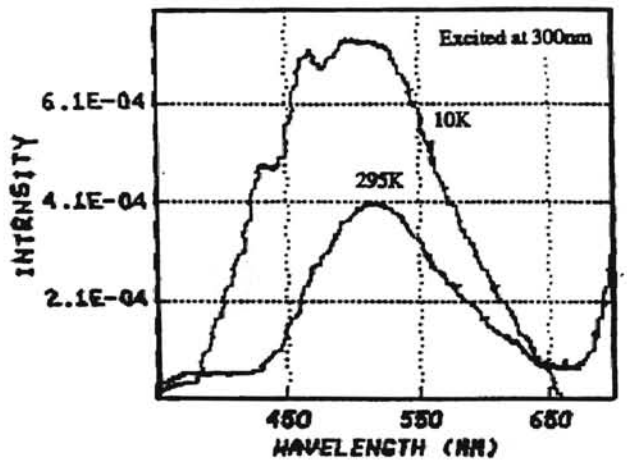
Table XXX (continued)

C22 C21 C20	118.7(16)
C23 C22 C21	123.0(18)
C24 C23 C22	119.0(17)
C23 C24 C25	120.0(16)
C23 C24 C26	121.6(19)
C25 C24 C26	118.4(18)
C20 C25 C24	119.6(15)
C121 C120 C125	121.8(16)
C121 C120 P1	116.9(14)
C125 C120 P1	121.0(13)
C120 C121 C122	117.6(18)
C123 C122 C121	120.6(19)
C122 C123 C124	120.5(20)
C123 C124 C125	121.0(20)
C123 C124 C126	119.3(20)
C125 C124 C126	119.7(20)
C124 C125 C120	118.4(17)
C321 C320 C325	117.8(15)
C321 C320 P3	125.5(13)
C325 C320 P3	116.7(12)
C320 C321 C322	121.0(16)
C323 C322 C321	120.4(15)
C324 C323 C322	120.9(17)
C323 C324 C325	118.5(17)
C323 C324 C326	120.9(18)
C325 C324 C326	120.3(16)
C320 C325 C324	121.2(15)

P(*p*-tol)$_3$



[CuIP(*p*-tol)$_3$]$_4$



[CuBrP(*p*-tol)$_3$]$_4$

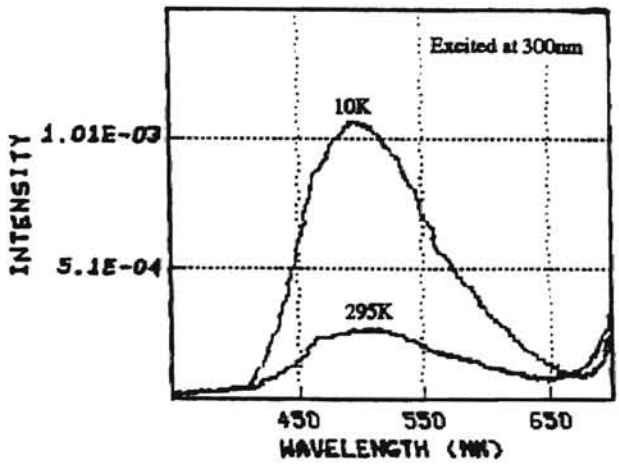


Figure 15. Emission Spectra of P(C_6H_4Me-*p*)$_3$, [CuIP(C_6H_4Me-*p*)3]4 and [CuBrP(C_6H_4Me-*p*)3]4

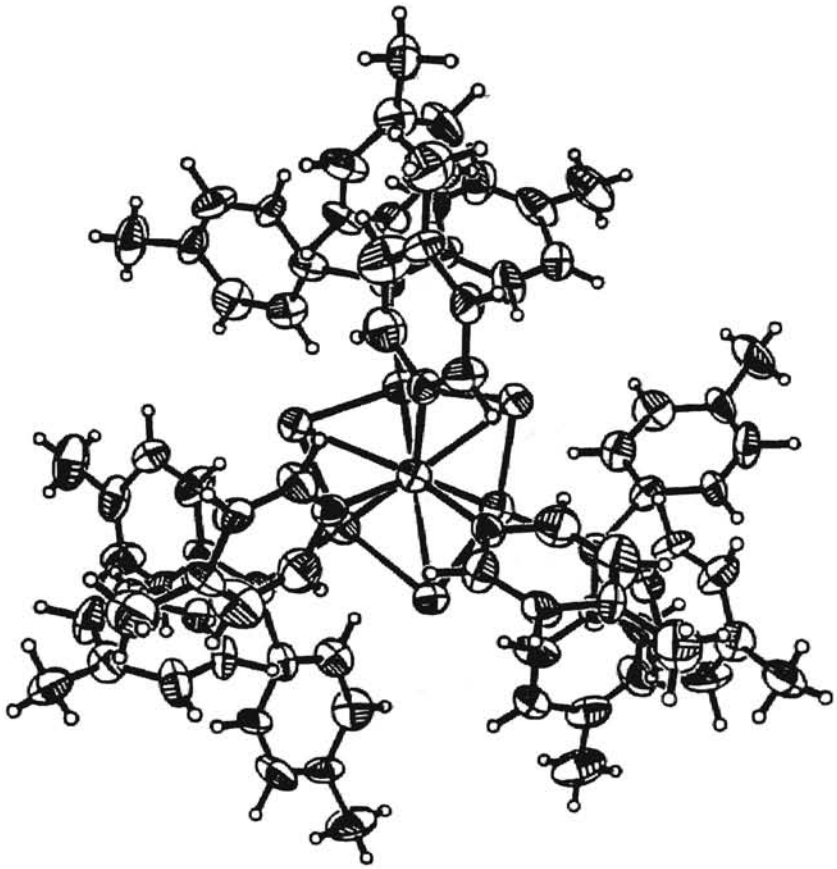


Figure 16. Projection view of [CuIP(C_6H_4Me-*p*)3]4

TABLE XXXI

CRYSTAL DATA FOR [CuIP(C_6H_4Me-*p*)$_3$]$_4$

Formula	$CuIPC_{21}H_{21}$
MWT	494.79
a	17.0690(10) Å
b	17.0690(10)
c	52.761(6)
α	90.0°
β	90.0
γ	120.0
V	13313.5(19) $Å^3$
F (000)	1464
μMoK_a	35.40 cm^{-1}
λMoK_a	0.71073
D_{calc}	0.370 Mg m^{-3}
Z	6
Independent Refl.	3875
Obs. Refl. ($F>4.0\sigma(F)$)	1466
R/R_w	7.81/13.48%
Space Group	R-3
Octants Meas.	$-1 \leq h \leq 18, -18 \leq k \leq 1,$ $-1 \leq l \leq 56$

TABLE XXXII

POSITIONAL PARAMETERS FOR
[CuIP(C_6H_4Me-*p*)3]4

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.5428(1)	1.1855(1)	0.1196(1)
I2	0.6667	1.3333	0.0521
Cu1	0.6720(2)	1.2318(2)	0.0906(1)
Cu2	0.6667	1.3333	0.1400(1)
P1	0.6780(4)	1.1087(4)	0.0781(1)
P2	0.6667	1.3333	0.1824(2)
C10	0.6638(15)	1.0335(15)	0.1033(4)
C11	0.5963(16)	0.9485(17)	0.1045(4)
C12	0.5882(16)	0.8982(16)	0.1259(5)
C13	0.6480(18)	0.9238(18)	0.1458(4)
C14	0.7184(19)	1.0065(16)	0.1427(5)
C15	0.7284(16)	1.0655(14)	0.1232(5)
C16	0.6323(13)	0.8584(14)	0.1680(4)
C20	0.5947(15)	1.0322(15)	0.0553(4)
C21	0.5113(15)	1.0320(15)	0.0559(4)
C22	0.4394(15)	0.9717(17)	0.0393(5)
C23	0.4581(20)	0.9093(16)	0.0247(4)
C24	0.5361(20)	0.9134(19)	0.0259(5)
C25	0.6022(15)	0.9703(17)	0.0417(5)
C26	0.3758(18)	0.8457(16)	0.0082(4)
C30	0.7823(15)	1.1301(13)	0.0633(3)
C31	0.8205(17)	1.1986(16)	0.0444(4)
C33	0.9439(14)	1.1692(18)	0.0367(5)
C32	0.8973(17)	1.2159(16)	0.0311(4)
C34	0.9057(20)	1.1061(17)	0.0554(5)
C35	0.8278(14)	1.0849(15)	0.0670(4)
C36	1.0317(14)	1.1978(18)	0.0225(4)
C40	0.7723(12)	1.4164(13)	0.1981(4)
C41	0.8048(14)	1.4005(14)	0.2198(4)
C43	0.9241(14)	1.5534(14)	0.2214(5)
C42	0.8812(15)	1.4673(15)	0.2305(4)
C44	0.8939(21)	1.5701(19)	0.2000(5)
C45	0.8172(17)	1.5024(18)	0.1870(5)
C46	1.0078(17)	1.6245(16)	0.2343(4)
C102	0.3338(54)	0.7363(53)	0.0945(15)
C103	0.2420(54)	0.6156(53)	0.0807(15)
C105	0.3973(52)	0.6842(60)	0.0730(14)
C107	0.3333	0.6667	0.1135(56)

TABLE XXXIII

HYDROGEN POSITIONAL PARAMETERS FOR
[CuIP(C_6H_4Me-*p*)3]4

ATOM	x	y	z
H11A	0.5517(16)	0.9245(17)	0.0912(4)
H12A	0.5380(16)	0.8377(16)	0.1276(5)
H15A	0.7774(16)	1.1267(14)	0.1218(5)
H16A	0.6794(13)	0.8856(14)	0.1805(4)
H16B	0.5750(13)	0.8405(14)	0.1759(4)
H16C	0.6316(13)	0.8063(14)	0.1610(4)
H14A	0.7647(19)	1.0301(16)	0.1554(5)
H21A	0.5052(15)	1.0709(15)	0.0679(4)
H22A	0.3842(15)	0.9736(17)	0.0380(5)
H24A	0.5414(20)	0.8706(19)	0.0153(5)
H25A	0.6585(15)	0.9706(17)	0.0414(5)
H26A	0.3925(18)	0.8074(16)	-0.0009(4)
H26B	0.3246(18)	0.8092(16)	0.0188(4)
H26C	0.3604(18)	0.8785(16)	-0.0037(4)
H31A	0.7909(17)	1.2318(16)	0.0398(4)
H32A	0.9227(17)	1.2612(16)	0.0181(4)
H34A	0.9356(20)	1.0722(17)	0.0588(5)
H35A	0.8032(14)	1.0361(15)	0.0790(4)
H36A	1.0476(14)	1.2461(18)	0.0107(4)
H36B	1.0792(14)	1.2159(18)	0.0348(4)
H36C	1.0236(14)	1.1451(18)	0.0137(4)
H41A	0.7731(14)	1.3412(14)	0.2271(4)
H42A	0.9054(15)	1.4551(15)	0.2455(4)
H44A	0.9299(21)	1.6294(19)	0.1929(5)
H45A	0.7956(17)	1.5161(18)	0.1717(5)
H46A	1.0302(17)	1.6813(16)	0.2256(4)
H46B	0.9914(17)	1.6302(16)	0.2513(4)
H46C	1.0539(17)	1.6080(16)	0.2347(4)

TABLE XXXIV

ANISOTROPIC THERMAL PARAMETERS FOR
$[CuIP(C_6H_4Me\text{-}p)_3]_4$

ATOM	U11	U22	U33	U12	U13	U23
I1	0.071(1)	0.069(1)	0.086(1)	0.0016(8)	0.0039(8)	0.0302(8)
Cu1	0.091(2)	0.081(2)	0.105(2)	-0.007(2)	0.001(2)	0.047(2)
P1	0.079(4)	0.070(4)	0.082(4)	-0.001(3)	0.004(3)	0.039(3)
C40	0.070(13)	0.061(14)	0.072(13)	0.013(11)	0.005(12)	0.037(12)
C16	0.063(15)	0.121(19)	0.110(18)	0.010(17)	-0.001(13)	0.038(14)
C10	0.078(15)	0.066(15)	0.091(17)	-0.039(14)	-0.027(14)	0.035(13)
C41	0.082(16)	0.070(15)	0.078(14)	0.018(13)	-0.020(13)	0.021(13)
C30	0.102(17)	0.061(14)	0.053(13)	-0.005(11)	0.002(12)	0.037(13)
C20	0.085(17)	0.096(18)	0.103(18)	0.037(15)	0.047(15)	0.062(15)
C31	0.120(21)	0.104(20)	0.084(17)	-0.001(15)	0.006(16)	0.064(17)
C43	0.073(16)	0.044(14)	0.110(19)	0.009(14)	0.005(15)	0.012(12)
C12	0.094(19)	0.070(17)	0.125(21)	-0.006(17)	-0.027(18)	-0.004(14)
C11	0.117(20)	0.093(19)	0.081(16)	-0.005(15)	-0.075(15)	0.049(17)
C15	0.091(18)	0.038(13)	0.153(24)	0.002(16)	-0.004(18)	0.007(13)
C42	0.090(17)	0.077(16)	0.098(16)	-0.004(14)	-0.048(14)	0.053(14)
C25	0.064(15)	0.113(20)	0.141(22)	-0.074(18)	-0.040(16)	0.039(16)
C13	0.104(20)	0.101(21)	0.069(16)	0.017(16)	0.024(15)	0.051(17)
C24	0.093(20)	0.148(26)	0.136(23)	-0.042(20)	0.014(19)	0.074(22)
C14	0.136(24)	0.059(16)	0.115(21)	0.014(16)	0.033(18)	0.041(17)
C23	0.117(23)	0.073(17)	0.081(17)	-0.031(14)	0.011(17)	0.012(17)
C35	0.067(15)	0.089(17)	0.142(21)	0.011(15)	0.026(15)	0.057(14)
C33	0.067(16)	0.112(20)	0.101(19)	-0.046(16)	-0.015(14)	0.061(16)
C22	0.069(17)	0.102(20)	0.178(27)	-0.008(20)	-0.016(18)	0.038(16)
C32	0.116(21)	0.125(21)	0.067(15)	0.008(14)	0.050(15)	0.058(19)
C21	0.073(16)	0.106(19)	0.091(17)	-0.056(15)	-0.011(14)	0.016(15)
C46	0.155(26)	0.116(22)	0.136(23)	-0.001(19)	-0.036(20)	0.064(21)
C34	0.144(26)	0.119(22)	0.124(21)	0.038(18)	0.026(19)	0.104(20)
C26	0.170(28)	0.100(20)	0.108(19)	-0.021(17)	-0.006(19)	0.011(20)
C44	0.163(29)	0.113(23)	0.086(18)	0.036(17)	-0.018(19)	0.049(22)
C45	0.109(21)	0.115(22)	0.116(20)	0.015(19)	-0.031(18)	0.060(18)
C36	0.087(18)	0.201(30)	0.163(24)	-0.031(22)	0.019(18)	0.085(20)
Cu2	0.090(2)	0.090(2)	0.085(3)	0.000	0.000	0.0449(11)
I2	0.076(1)	0.0762(11)	0.074(2)	0.000	0.000	0.0381(5)
P2	0.064(4)	0.064(4)	0.078(6)	0.000	0.000	0.032(2)

The anisotropic displacement exponent takes the form:

$-2\pi^2(h^2a^{*2}U_{11} + ..2hka^*b^*U_{12})$

TABLE XXXV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
[CuIP(C_6H_4Me-*p*)$_3$]$_4$

I1 Cu1	2.674(3)	Cu1 I1 Cu1	70.10(12)
I1 Cu1	2.697(3)	Cu1 I1 Cu2	71.91(9)
I1 Cu2	2.698(2)	Cu1 I1 Cu2	71.54(9)
Cu1 P1	2.253(6)	P1 Cu1 I1	111.0(2)
Cu1 I1	2.674(3)	P1 Cu1 I1	111.3(2)
Cu1 I2	2.705(3)	I1 Cu1 I1	105.81(10)
P1 C10	1.78(2)	P1 Cu1 I2	114.0(2)
P1 C30	1.81(2)	I1 Cu1 I2	107.45(10)
P1 C20	1.82(3)	I1 Cu1 I2	106.77(10)
C40 C41	1.35(2)	C10 P1 C30	103.5(10)
C40 C45	1.40(3)	C10 P1 C20	101.6(10)
C40 P2	1.84(2)	C30 P1 C20	101.4(9)
C16 C13	1.55(3)	C10 P1 Cu1	113.5(7)
C10 C11	1.33(3)	C30 P1 Cu1	116.0(7)
C10 C15	1.42(3)	C20 P1 Cu1	118.7(8)
C41 C42	1.35(2)	C41 C40 C45	120.0(20)
C30 C35	1.36(2)	C41 C40 P2	124.5(16)
C30 C31	1.42(3)	C45 C40 P2	115.4(17)
C20 C25	1.33(3)	C11 C10 C15	117.9(21)
C20 C21	1.42(3)	C11 C10 P1	123.6(17)
C31 C32	1.38(3)	C15 C10 P1	118.5(18)
C43 C44	1.33(3)	C42 C41 C40	120.2(19)
C43 C42	1.36(2)	C35 C30 C31	114.2(21)
C43 C46	1.50(3)	C35 C30 P1	127.7(17)
C12 C13	1.37(3)	C31 C30 P1	118.0(18)
C12 C11	1.39(3)	C25 C20 C21	120.2(23)
C15 C14	1.39(3)	C25 C20 P1	125.0(18)
C25 C24	1.35(3)	C21 C20 P1	114.0(17)
C13 C14	1.33(3)	C32 C31 C30	121.8(22)
C24 C23	1.30(3)	C44 C43 C42	118.3(22)
C23 C22	1.47(3)	C44 C43 C46	121.9(22)
C23 C26	1.55(3)	C42 C43 C46	119.6(23)
C35 C34	1.34(3)	C13 C12 C11	126.8(22)
C33 C34	1.37(3)	C10 C11 C12	118.6(20)
C33 C32	1.41(3)	C14 C15 C10	118.5(21)
C33 C36	1.52(3)	C41 C42 C43	122.1(20)
C22 C21	1.44(3)	C20 C25 C24	121.7(24)
C44 C45	1.42(3)	C14 C13 C12	112.0(23)
Cu2 P2	2.239(10)	C14 C13 C16	126.9(24)
Cu2 I1	2.698(2)	C12 C13 C16	121.0(24)
Cu2 I1	2.698(2)	C23 C24 C25	122.4(25)

Table XXXV (continued)

I2 Cu1	2.705(3)	C13 C14 C15	125.6(26)
I2 Cu1	2.705(3)	C24 C23 C22	121.4(24)
P2 C40	1.84(2)	C24 C23 C26	127.8(27)
P2 C40	1.84(2)	C22 C23 C26	110.8(27)
C103 C102	0.94(9)	C34 C35 C30	123.8(22)
C103 C105	0.98(10)	C34 C33 C32	114.5(21)
C103 C105	1.56(11)	C34 C33 C36	127.9(25)
C103 C102	2.00(10)	C32 C33 C36	117.5(25)
C105 C103	0.98(10)	C21 C22 C23	114.9(22)
C105 C102	1.19(10)	C31 C32 C33	121.1(22)
C105 C103	1.56(11)	C20 C21 C22	118.8(22)
C105 C105	1.69(13)	C35 C34 C33	124.2(22)
C105 C105	1.69(13)	C43 C44 C45	122.5(25)
C105 C102	2.05(11)	C40 C45 C44	116.6(22)
C102 C103	0.94(9)	P2 Cu2 I1	113.53(9)
C102 C105	1.19(10)	P2 Cu2 I1	113.53(9)
C102 C107	1.55(18)	I1 Cu2 I1	105.12(10)
C102 C102	2.05(13)	P2 Cu2 I1	113.53(9)
C102 C102	2.05(13)	I1 Cu2 I1	105.12(10)
C107 C102	1.55(18)	I1 Cu2 I1	105.12(10)
C107 C102	1.55(18)	Cu1 I2 Cu1	69.53(8)
		Cu1 I2 Cu1	69.53(8)
		Cu1 I2 Cu1	69.53(8)
		C40 P2 C40	101.3(8)
		C40 P2 C40	101.3(8)
		C40 P2 C40	101.3(8)
		C40 P2 Cu2	116.8(6)
		C40 P2 Cu2	116.8(6)
		C40 P2 Cu2	116.8(6)
		C102 C103 C105	76.5(87)
		C102 C103 C105	108.2(92)
		C105 C103 C105	80.0(95)
		C102 C103 C102	79.7(87)
		C105 C103 C102	94.8(79)
		C105 C103 C102	36.5(38)
		C103 C105 C102	50.0(64)
		C103 C105 C103	133.3(100)
		C102 C105 C103	92.5(77)
		C103 C105 C105	65.0(86)
		C102 C105 C105	89.1(65)
		C103 C105 C105	91.9(47)
		C103 C105 C105	119.2(79)
		C102 C105 C105	104.7(52)
		C103 C105 C105	35.0(45)
		C105 C105 C105	60.00(2)
		C103 C105 C102	107.8(80)

Table XXXV (continued)

C102 C105 C102	73.1(66)
C103 C105 C102	25.7(36)
C105 C105 C102	75.2(39)
C105 C105 C102	35.4(33)
C103 C102 C105	53.6(66)
C103 C102 C107	122.0(100)
C105 C102 C107	117.3(100)
C103 C102 C103	99.4(90)
C105 C102 C103	51.0(60)
C107 C102 C103	75.2(73)
C103 C102 C102	110.2(70)
C105 C102 C102	73.2(58)
C107 C102 C102	48.6(66)
C103 C102 C102	26.7(30)
C103 C102 C102	73.6(80)
C105 C102 C102	86.2(52)
C107 C102 C102	48.6(65)
C103 C102 C102	77.4(34)
C102 C102 C102	60.00(2)
C103 C102 C105	46.1(68)
C105 C102 C105	55.5(62)
C107 C102 C105	80.0(89)
C103 C102 C105	70.4(39)
C102 C102 C105	68.2(33)
C102 C102 C105	33.7(29)
C102 C107 C102	82.8(100)
C102 C107 C102	82.8(100)
C102 C107 C102	82.8(100)

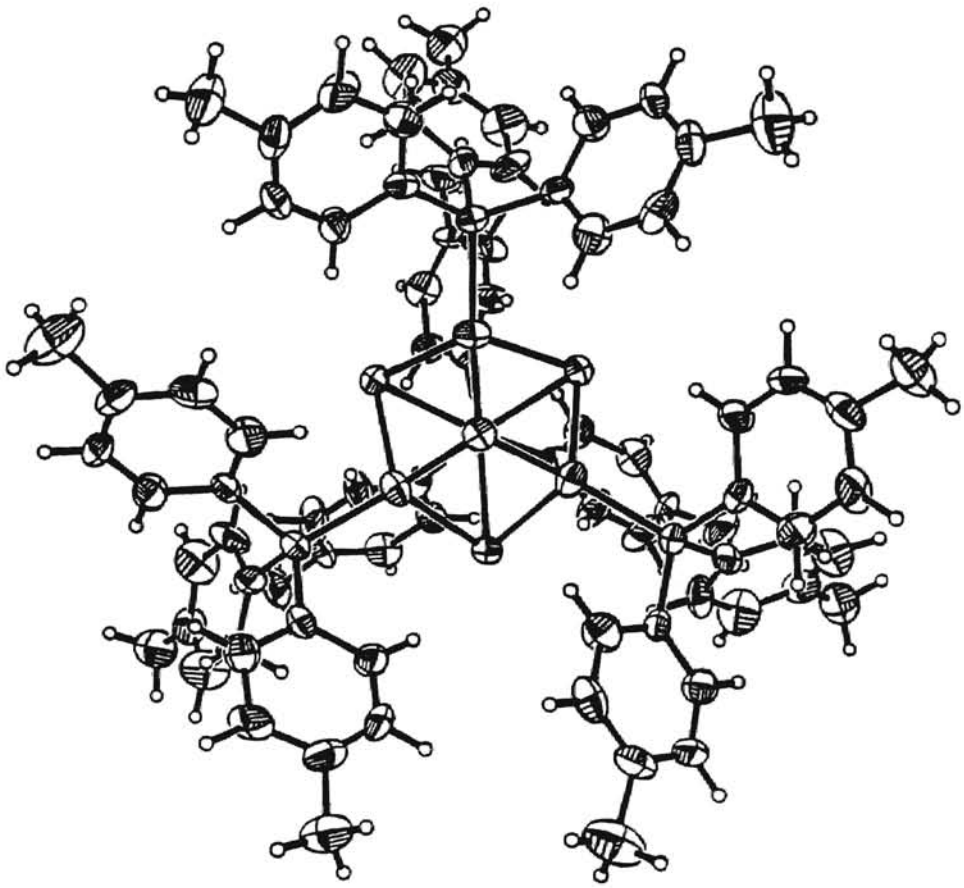


Figure 17. Projection view of [CuBrP(C_6H_4Me-*p*)$_3$]$_4$

TABLE XXXVI

CRYSTAL DATA FOR $[CuBrP(C_6H_4Me\text{-}p)_3]_4$

Formula	$CuBrPC_{21}H_{21}$
MWT	1794.2
a	17.033(2) Å
b	17.033(2)
c	51.785(9)
α	90.0°
β	90.0
γ	120.0
V	13011(5) $Å^3$
F (000)	5442
μMoK_a	3.089
λMoK_a	0.71073
D_{calc}	1.374 Mg m^{-3}
Z	6
Independent Refl.	3800
Obs. Refl. ($F>5.1\sigma(F)$)	1490
R/R_w	5.92/6.13%
Space Group	R-3
Octants Meas.	$-1 \le h \le 18, -18 \le k \le 1,$ $-1 \le l \le 55$

TABLE XXXVII

POSITIONAL PARAMETERS FOR
[CuBrP(C_6H_4Me-*p*)3]4

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu1	3350(2)	5572(1)	4099(1)
Cu2	3333	6667	3592(1)
Br1	2014(1)	5339(1)	3823(1)
Br2	3333	6667	4437(1)
P1	3266(3)	4281(3)	4219(1)
P2	3333	6667	3162(1)
C20	4109(12)	4357(11)	4441(3)
C30	2212(10)	3515(11)	4384(3)
C35	1752(13)	2568(12)	4342(3)
C50	3343(12)	3632(10)	3957(3)
C31	1842(14)	3850(14)	4554(3)
C33	630(12)	2351(18)	4641(4)
C21	4966(13)	5186(12)	4454(3)
C52	4039(16)	2900(16)	3716(4)
C34	994(13)	2018(12)	4473(4)
C25	4035(14)	3668(12)	4600(4)
C51	3994(13)	3402(15)	3926(5)
C55	2730(13)	3329(13)	3754(4)
C23	5566(14)	4613(19)	4757(4)
C32	1068(16)	3285(19)	4685(4)
C54	2765(18)	2818(15)	3555(4)
C53	3450(17)	2666(13)	3535(4)
C22	5624(13)	5254(13)	4598(4)
C56	3473(13)	2114(13)	3317(4)
C24	4774(16)	3774(16)	4757(3)
C26	6303(12)	4619(13)	4922(3)
C36	-296(12)	1747(15)	4784(4)
C110	4203(10)	7676(11)	3009(3)
C111	4076(12)	8068(11)	2799(3)
C115A	5059(14)	8173(14)	3127(4)
C112	4813(16)	8831(13)	2685(3)
C113	5659(13)	9243(12)	2784(4)
C116	6374(11)	10044(12)	2632(3)
C115B	5733(15)	8853(17)	3002(5)

TABLE XXXVIII

HYDROGEN POSITIONAL PARAMETERS FOR
[CuBrP(C_6H_4Me-*p*)$_3$]$_4$

ATOM	x	y	z
H35A	1998	2319	4221
H31A	2139	4493	4581
H21A	5049	5711	4362
H52A	4496	2730	3701
H34A	678	1374	4446
H25A	3458	3119	4606
H51A	3939	3042	4074
H51B	4572	3948	3936
H55A	2272	3500	3764
H32A	832	3531	4980
H54A	2277	2580	3433
H22A	6203	5280	4598
H56A	4023	2091	3333
H56B	2962	1512	3331
H56C	3462	2364	3152
H24A	4686	3265	4858
H26A	6126	4068	5016
H26B	6826	4765	4818
H26C	6446	5103	5042
H36A	-448	2097	4897
H36B	-771	1438	4659
H36C	-225	1310	4883
H11A	3482	7810	2724
H11B	5131	7996	3298
H11C	4730	9070	2526
H11D	6944	10292	2720
H11E	6429	9845	2463
H11F	6202	10500	2616
H11G	6326	9107	3077

TABLE XXXIX

ANISOTROPIC THERMAL PARAMETERS FOR
$[CuBrP(C_6H_4Me\text{-}p)_3]_4$

ATOM	U11	U22	U33	U12	U13	U23
Cu1	83(2)	58(1)	105(2)	40(1)	-3(1)	13(1)
Cu2	89(2)	89(2)	63(2)	44(1)	0	0
Br1	49(1)	50(1)	75(1)	20(1)	-6(1)	-4(1)
Br2	60(1)	60(1)	62(2)	30(1)	0	0
P1	59(3)	50(3)	77(3)	33(3)	-3(2)	7(2)
P2	66(3)	66(3)	57(5)	33(2)	0	0
C20	73(13)	47(11)	60(10)	37(11)	5(9)	-2(9)
C30	60(12)	52(12)	66(11)	36(11)	5(9)	7(9)
C35	73(14)	67(14)	77(12)	33(12)	6(11)	-10(11)
C50	53(12)	67(12)	64(12)	31(10)	-13(10)	21(9)
C31	87(16)	92(16)	77(14)	46(14)	27(11)	5(12)
C33	45(13)	103(19)	83(15)	23(14)	2(12)	33(14)
C21	58(13)	71(15)	110(16)	26(12)	-21(12)	24(11)
C52	124(20)	148(22)	65(13)	85(18)	-22(14)	-47(14)
C34	52(13)	59(13)	122(16)	19(12)	33(12)	16(13)
C25	87(15)	79(14)	108(15)	39(12)	19(13)	45(13)
C51	59(14)	113(19)	164(24)	35(14)	-31(15)	9(17)
C55	107(17)	106(17)	88(14)	83(15)	-3(14)	25(13)
C23	56(15)	105(19)	89(16)	43(16)	-19(12)	-32(14)
C32	88(17)	127(21)	94(15)	77(17)	9(14)	-14(15)
C54	144(24)	122(20)	76(16)	74(19)	-24(15)	-31(14)
C53	88(18)	70(14)	89(17)	37(14)	39(15)	-14(12)
C22	49(14)	55(14)	127(18)	6(11)	-1(13)	19(13)
C56	114(18)	129(18)	113(16)	70(15)	7(13)	11(15)
C24	95(17)	118(19)	76(13)	68(17)	-6(12)	39(12)
C26	82(15)	154(20)	114(17)	65(15)	-5(13)	15(14)
C36	90(18)	191(25)	109(16)	41(18)	7(15)	28(16)
C110	47(11)	74(12)	44(9)	31(10)	-7(8)	-6(9)
C111	71(13)	64(13)	69(12)	27(11)	-3(11)	13(10)
C115A	67(14)	88(15)	102(15)	12(13)	-16(14)	40(13)
C112	110(18)	90(15)	45(10)	49(14)	21(12)	31(11)
C113	47(14)	50(13)	111(17)	6(11)	-24(13)	-19(12)
C116	52(13)	92(16)	157(20)	11(12)	20(13)	34(14)
C115B	63(16)	142(23)	132(19)	27(16)	-42(15)	31(17)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE XL

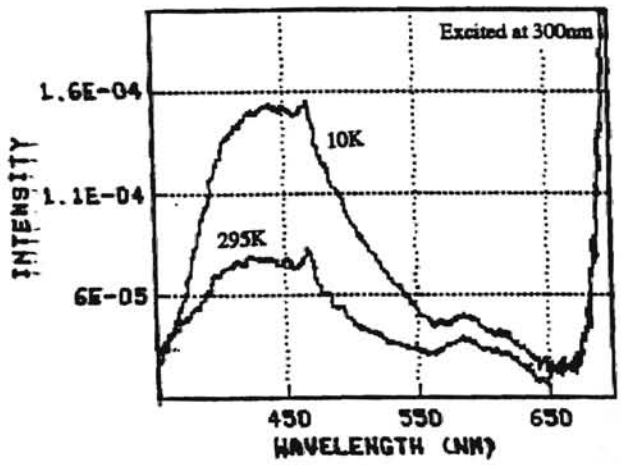
BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[CuIP(C_6H_4Me\text{-}p)_3]_4$

Cu1-Br1	2.547 (3)	Br1-Cu1-Br2	99.4(1)
Cu1-Br2	2.567 (3)	Br1-Cu1-P1	113.1(1)
Cu1-P1	2.221 (6)	Br2-Cu1-P	1120.7(1)
Cu1-Br1A	2.526 (2)	Br1-Cu1-Br1A	100.7(1)
Cu2-Br1	2.552 (2)	Br2-Cu1-Br1A	100.0(1)
Cu2-P2	2.224 (8)	P1-Cu1-Br1A	119.4(2)
Cu2-Br1A	2.553 (2)	Br1-Cu2-P2	117.9(1)
Cu2-Br1B	2.551 (2)	Br1-Cu2-Br1A	99.8(1)
Br1-Cu1B	2.526 (3)	P2-Cu2-Br1A	117.9(1)
Br2-Cu1A	2.567 (3)	Br1-Cu2-Br1B	99.9(1)
Br2-Cu1B	2.566 (3)	P2-Cu2-Br1B	117.9(1)
P1-C20	1.791 (19)	Br1A-Cu2-Br1B	99.8(1)
P1-C30	1.818 (14)	Cu1-Br1-Cu(2)	78.7(1)
P1-C50	1.796 (19)	Cu1-Br1-Cu1B	79.8(1)
P2-C110	1.798 (14)	Cu2-Br1-Cu1B	79.0(1)
P2-C11A	1.797 (19)	Cu1-Br2-Cu1A	78.6(1)
P2-C11B	1.799 (9)	Cu1-Br2-Cu1B	78.7(1)
C20-C21	1.439 (20)	Cu1A-Br2-Cu1B	78.7(1)
C20-C25	1.388 (28)	Cu1-P1-C20	117.1(6)
C30-C35	1.413 (25)	Cu1-P1-C30	113.2(7)
C30-C31	1.364 (32)	C20-P1-C30	102.7(7)
C35-C34	1.340 (24)	Cu1-P1-C50	114.2(6)
C50-C51	1.358 (37)	C20-P1-C50	103.0(10)
C50-C55	1.387 (26)	C30-P1-C50	105.2(7)
C31-C32	1.362 (28)	Cu2-P2-C110	116.2(5)
C33-C34	1.349 (36)	Cu2-P2-C11A	116.2(5)
C33-C32	1.396 (39)	C110-P2-C11A	102.0(6)
C33-C36	1.571 (25)	Cu2-P2-C11B	116.2(5)
C21-C22	1.302 (32)	C110-P2-C11B	102.0(7)
C52-C55	1.406 (36)	C11A-P2-C11B	102.0(6)
C52-C53	1.284 (34)	P1-C20-C21	119.0(14)
C25-C24	1.430 (34)	P1-C20-C25	126.1(12)
C55-C54	1.370 (34)	C21-C20-C25	114.8(17)
C23-C22	1.334 (37)	P1-C30-C35	122.1(15)
C23-C24	1.391 (28)	P1-C30-C31	120.0(13)
C23-C26	1.513 (34)	C35-C30-C31	117.9(15)
C54-C53	1.319 (47)	C30-C35-C34	120.7(20)
C53-C56	1.483 (33)	P1-C50-C51	126.1(15)
C110-C111	1.351 (26)	P1-C50-C55	121.9(19)
C110-C115A	1.408 (25)	C51-C50-C55	111.9(19)
C111-C112	1.406 (22)	C30-C31-C32	120.8(21)
C112-C113	1.349 (30)	C34-C33-C32	119.2(18)

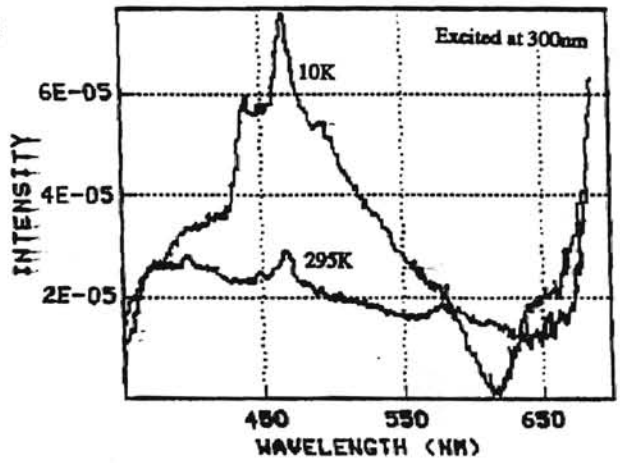
Table XL (continued)

C113-C116	1.519 (23)	C34-C33-C36	123.3(21)
C113-C115B	1.345 (35)	C32-C33-C36	117.4(23)
		C20-C21-C22	121.4(19)
		C51-C52-C53	118.8(29)
		C35-C34-C33	121.2(19)
		C20-C25-C24	121.9(15)
		C50-C51-C52	124.7(21)
		C50-C52-C54	122.8(25)
		C22-C23-C24	118.4(22)
		C22-C23-C26	128.5(17)
		C24-C23-C26	112.6(24)
		C31-C32-C33	120.1(26)
		C55-C54-C53	120.6(22)
		C52-C53-C54	120.8(25)
		C52-C53-C56	119.4(28)
		C54-C53-C56	119.4(21)
		C21-C22-C23	125.0(16)
		C25-C24-C23	118.2(23)
		P2-C110-C111	124.7(12)
		P2-C110-C115	119.6(13)
		C111-C110-C115	115.3(14)
		C110-C111-C112	120.3(17)
		C110-C115-C115	119.8(20)
		C111-C112-C113	123.3(19)
		C112-C113-C116	115.9(19)
		C112-C113-C115	113.7(16)
		C116-C113-C115	130.4(18)
		C115A-C115B-C113	126.0(22)

P(*o*-tol)$_3$



[CuIP(*o*-tol)$_3$]$_2$



[CuBrP(*o*-tol)$_3$]$_2$

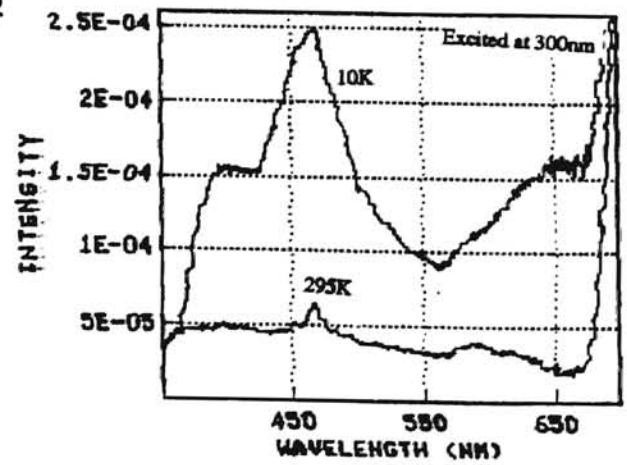


Figure 18. Emission Spectra of P(C_6H_4Me-*o*)$_3$, [CuIP(C_6H_4Me-*o*)$_3$]$_2$•[C_6H_4Me] and [CuBrP(C_6H_4Me-*o*)$_3$]$_2$

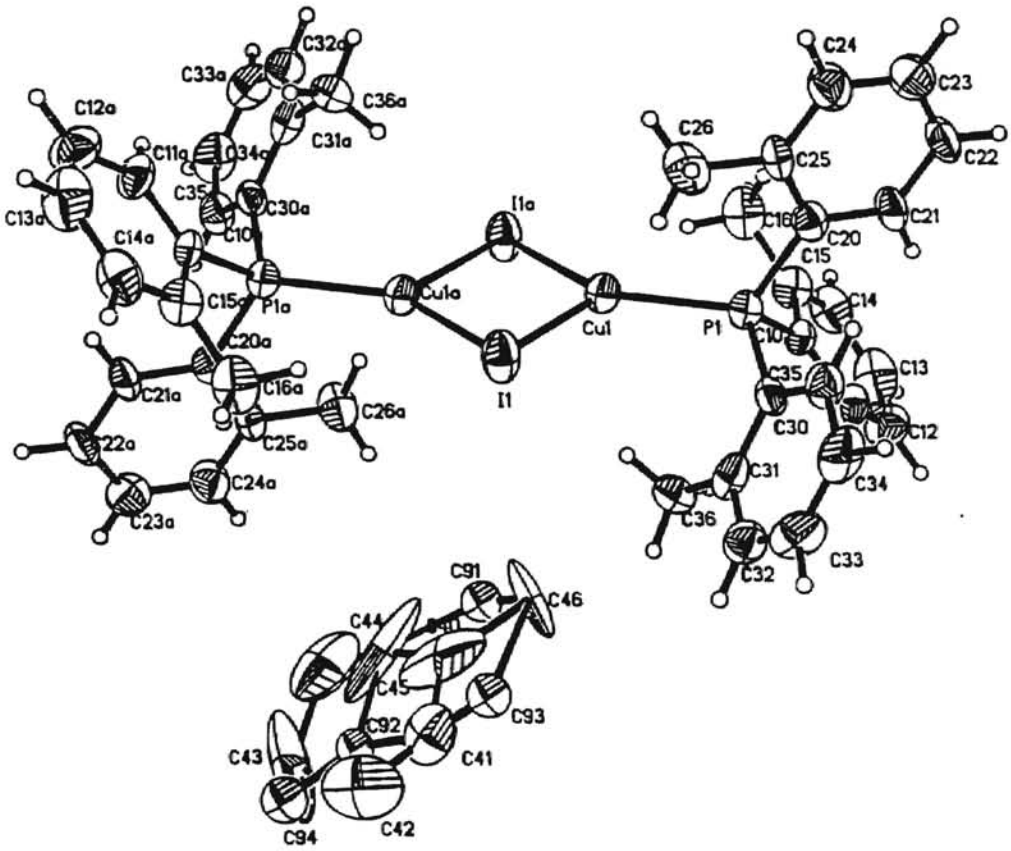


Figure 19. Projection view of [CuIP(C_6H_4Me-*o*)3]2 •[C_6H_4Me]

TABLE XLI

CRYSTAL DATA FOR $[Cu_2I_2(P(C_6H_4Me\text{-}o)_3)_2][C_7H_8]$

Formula	$CuIPC_{21}H_{21}$
MWT	494.79
a	11.0540(10) Å
b	20.149(2)
c	12.1930(10)
α	90.0°
β	103.87
γ	90.0
V	2636.5(4) $Å^3$
F (000)	1464
μMoK_a	3.089
λMoK_a	0.71073
D_{calc}	1.870 Mg m^{-3}
Z	4
Independent Refl.	2463
Obs. Refl. ($F>4.0\sigma(F)$)	1466
R/R_w	5.37/11.56%
Space Group	$P2_1/n$
Octants Meas.	$-1 \leq h \leq 10, -1 \leq k \leq 19,$ $-11 \leq l \leq 11$

TABLE XLII

POSITIONAL PARAMETERS FOR
$[Cu_2I_2(P(C_6H_4Me\text{-}o)_3)_2][C_7H_8]$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.0149(7)	0.09518(4)	0.443(5)
Cu1	-0.1185(1)	-0.01512(7)	0.404(6)
P1	-0.276(9)	-0.0178(2)	0.251(6)
C10	-0.301(1)	-0.0941(6)	0.165(1)
C11	-0.303(1)	-0.0929(7)	0.052(1)
C12	-0.320(1)	-0.1482(11)	-0.012(1)
C13	-0.335(1)	-0.2070(10)	0.038(1)
C14	-0.336(1)	-0.2117(7)	0.150(1)
C15	-0.319(1)	-0.1552(7)	0.216(1)
C16	-0.321(1)	-0.1607(6)	0.337(1)
C20	-0.432(1)	-0.0019(6)	0.269(1)
C21	-0.535(1)	-0.0316(6)	0.201(1)
C22	-0.655(1)	-0.0229(8)	0.214(1)
C23	-0.673(1)	0.0181(8)	0.300(1)
C24	-0.572(1)	0.0470(8)	0.369(1)
C25	-0.454(1)	0.0382(7)	0.356(1)
C26	-0.349(1)	0.0753(7)	0.431(1)
C30	-0.254(1)	0.0478(6)	0.155(1)
C31	-0.140(1)	0.0511(7)	0.122(1)
C32	-0.121(1)	0.1055(9)	0.059(1)
C33	-0.206(2)	0.1534(9)	0.026(1)
C34	-0.318(1)	0.1501(8)	0.054(1)
C35	-0.339(1)	0.0973(7)	0.120(1)
C36	-0.038(1)	0.0014(7)	0.154(1)

TABLE XLIII

HYDROGEN POSITIONAL PARAMETERS FOR
$[Cu_2I_2(P(C_6H_4Me\text{-}o)_3)_2][C_7H_8]$

ATOM	x	y	z
H11A	-0.292(1)	-0.0508(7)	0.019(1)
H12A	-0.322(1)	-0.1466(11)	-0.092(1)
H13A	-0.340(1)	-0.2475(10)	-0.004(1)
H14A	-0.355(1)	-0.2535(7)	0.181(1)
H16A	-0.336(1)	-0.2059(6)	0.355(1)
H16B	-0.242(1)	-0.1466(6)	0.382(1)
H16C	-0.386(1)	-0.1328(6)	0.352(1)
H21A	-0.522(1)	-0.0585(6)	0.140(1)
H22A	-0.724(1)	-0.0446(8)	0.164(1)
H23A	-0.756(16)	0.0256(8)	0.308(1)
H24A	-0.587(1)	0.0728(8)	0.431(1)
H26A	-0.272(1)	0.0657(7)	0.412(1)
H26B	-0.365(1)	0.1222(7)	0.424(1)
H26C	-0.344(1)	0.0618(7)	0.508(1)
H32A	-0.046(1)	0.1079(9)	0.034(1)
H33A	-0.187(2)	0.1915(9)	-0.014(1)
H34A	-0.381(1)	0.1829(8)	0.027(1)
H35A	-0.416(1)	0.0958(7)	0.143(1)
H36A	0.032(1)	0.0145(7)	0.124(1)
H36B	-0.012(1)	-0.0030(7)	0.234(1)
H36C	-0.070(1)	-0.0403(7)	0.121(1)

TABLE XLIV

ANISOTROPIC THERMAL PARAMETERS FOR
$[Cu_2I_2(P(C_6H_4Me\text{-}o)_3)_2][C_7H_8]$

ATOM	U11	U22	U33	U12	U13	U23
I1	0.083(1)	0.066(6)	0.085(4)	0.0183(5)	-0.0139(5)	-0.013(1)
Cu1	0.063(1)	0.068(1)	0.057(1)	0.0034(8)	0.0034(8)	0.003(5)
P1	0.059(2)	0.05(4)	0.05(4)	0.000(2)	0.004(2)	-0.00(1)
C10	0.06(5)	0.07(1)	0.04(2)	-0.016(7)	0.004(7)	-0.02(8)
C11	0.09(1)	0.08(1)	0.06(1)	-0.026(9)	0.007(8)	-0.00(1)
C12	0.11(1)	0.12(1)	0.08(1)	-0.019(13)	0.029(10)	0.02(1)
C13	0.10(1)	0.09(1)	0.13(1)	-0.050(13)	0.006(14)	0.02(1)
C14	0.09(1)	0.06(1)	0.17(1)	-0.019(10)	0.014(11)	-0.02(7)
C15	0.08(1)	0.05(1)	0.08(1)	0.003(9)	0.010(9)	0.010(9)
C16	0.10(1)	0.04(1)	0.11(1)	0.019(8)	-0.001(10)	-0.01(1)
C20	0.06(1)	0.05(2)	0.06(2)	0.009(7)	0.006(8)	0.00(3)
C21	0.05(1)	0.07(4)	0.08(8)	-0.004(7)	0.000(9)	-0.02(1)
C22	0.04(1)	0.10(1)	0.09(1)	0.004(10)	0.001(9)	-0.02(1)
C23	0.08(1)	0.10(1)	0.09(1)	-0.001(10)	0.025(11)	0.02(1)
C24	0.07(1)	0.10(1)	0.09(1)	-0.013(9)	0.016(11)	0.01(1)
C25	0.04(1)	0.07(5)	0.07(1)	0.002(8)	-0.005(8)	-0.01(3)
C26	0.07(1)	0.10(1)	0.11(1)	-0.049(9)	0.017(10)	0.01(2)
C30	0.03(7)	0.06(3)	0.06(8)	-0.006(7)	0.004(7)	0.00(4)
C31	0.10(1)	0.06(1)	0.05(9)	-0.002(8)	-0.005(9)	-0.01(1)
C32	0.09(1)	0.08(1)	0.07(1)	0.006(9)	0.016(9)	-0.01(1)
C33	0.15(2)	0.07(1)	0.08(1)	0.001(10)	0.032(14)	-0.05(1)
C34	0.12(1)	0.07(1)	0.08(1)	0.039(9)	-0.005(11)	0.01(1)
C35	0.07(1)	0.07(8)	0.07(1)	0.016(8)	-0.001(8)	-0.01(1)
C36	0.06(1)	0.12(1)	0.08(1)	-0.007(9)	0.026(8)	-0.00(1)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE XLV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
$[Cu_2I_2(P(C_6H_4Me\text{-}o)_3)_2][C_7H_8]$

I1 Cu1	2.530(2)	Cu1 I1 Cu1	74.40(6)
I1 Cu1	2.647(2)	P1 Cu1 I1	136.77(11)
Cu1 P1	2.233(3)	P1 Cu1 I1	117.54(10)
Cu1 I1	2.530(2)	I1 Cu1 I1	105.60(6)
P1 C20	1.815(13)	C20 P1 C30	103.5(6)
P1 C30	1.823(13)	C20 P1 C10	102.0(6)
P1 C10	1.839(12)	C30 P1 C10	105.5(6)
C20 C21	1.38(2)	C20 P1 Cu1	117.9(5)
C20 C25	1.40(2)	C30 P1 Cu1	108.4(4)
C21 C22	1.38(2)	C10 P1 Cu1	118.0(4)
C22 C23	1.38(2)	C21 C20 C25	116.3(12)
C23 C24	1.35(2)	C21 C20 P1	121.1(11)
C24 C25	1.36(2)	C25 C20 P1	122.6(11)
C25 C26	1.50(2)	C20 C21 C22	123.5(13)
C30 C35	1.37(2)	C21 C22 C23	118.2(14)
C30 C31	1.41(2)	C24 C23 C22	119.3(15)
C31 C32	1.38(2)	C23 C24 C25	122.4(15)
C31 C36	1.49(2)	C24 C25 C20	120.4(13)
C32 C33	1.34(2)	C24 C25 C26	119.5(15)
C33 C34	1.37(2)	C20 C25 C26	120.0(13)
C34 C35	1.39(2)	C35 C30 C31	118.3(13)
C10 C11	1.37(2)	C35 C30 P1	122.3(11)
C10 C15	1.41(2)	C31 C30 P1	119.1(11)
C11 C12	1.35(2)	C32 C31 C30	117.2(14)
C12 C13	1.36(2)	C32 C31 C36	118.1(16)
C13 C14	1.38(2)	C30 C31 C36	124.6(13)
C14 C15	1.38(2)	C33 C32 C31	123.6(16)
C15 C16	1.49(2)	C32 C33 C34	119.9(17)
		C33 C34 C35	118.4(16)
		C30 C35 C34	122.6(14)
		C11 C10 C15	118.8(12)
		C11 C10 P1	121.2(11)
		C15 C10 P1	120.0(10)
		C12 C11 C10	122.6(14)
		C11 C12 C13	117.8(15)
		C12 C13 C14	122.7(16)
		C15 C14 C13	119.0(15)
		C14 C15 C10	119.0(13)
		C14 C15 C16	118.7(14)
		C10 C15 C16	122.3(12)

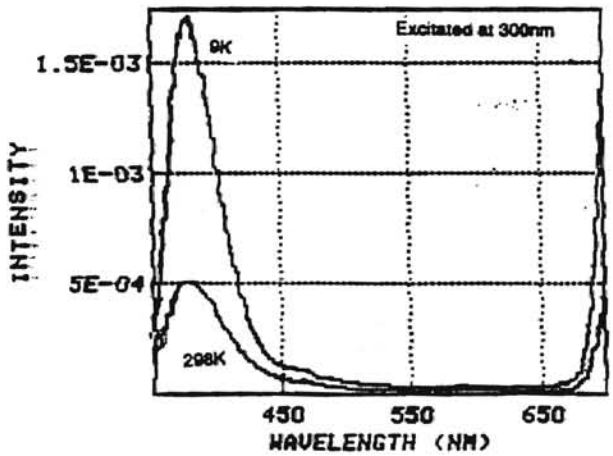


Figure 20. Emission Spectra of $Cu_2I_2(P(C_6H_{11})_3)_2$

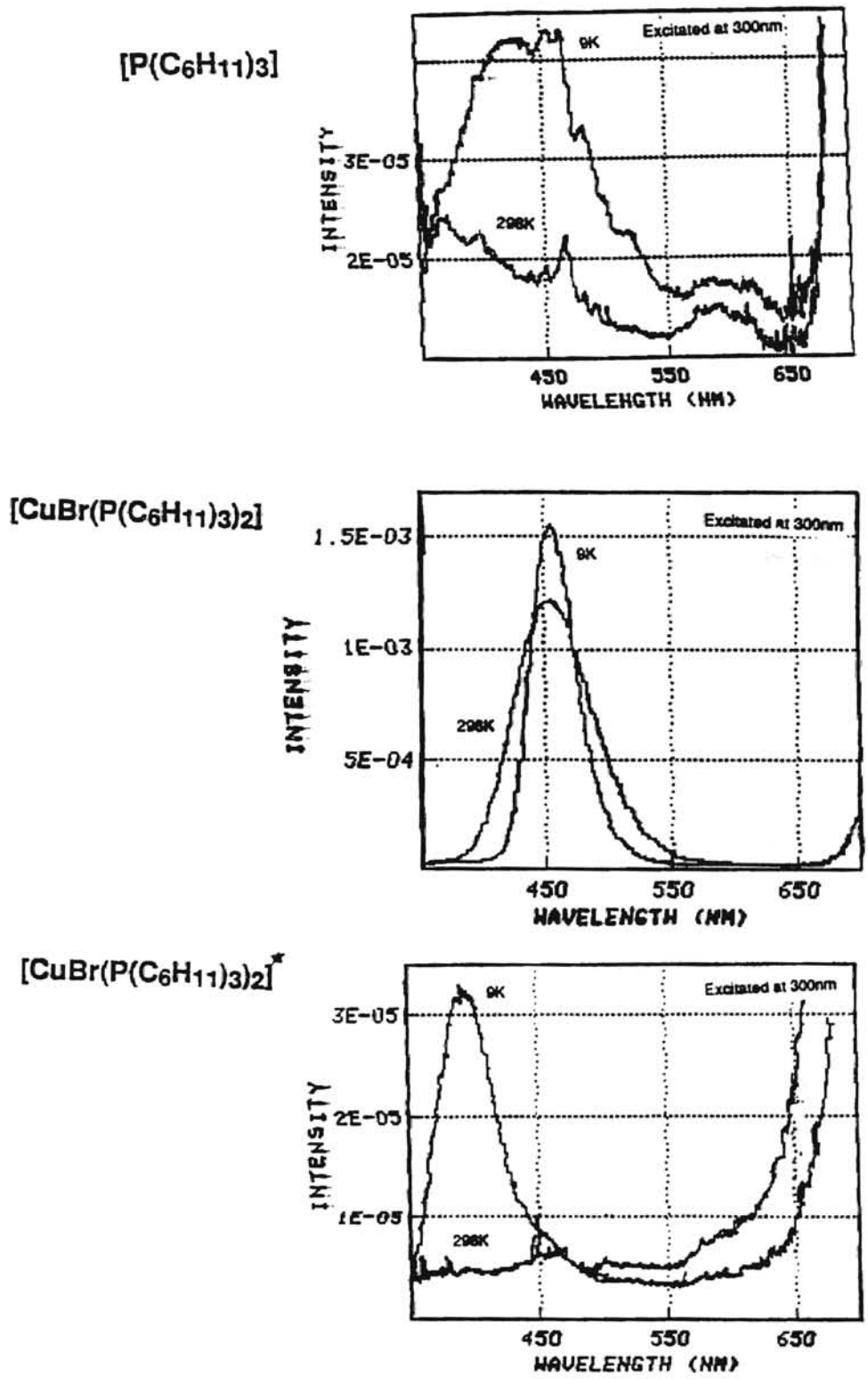


Figure 21. Emission Spectra of $P(C_6H_{11})_3$, $[CuBr(P(C_6H_{11})_3)_2]$ and $[CuBr(P(C_6H_{11})_3)_2]^*$

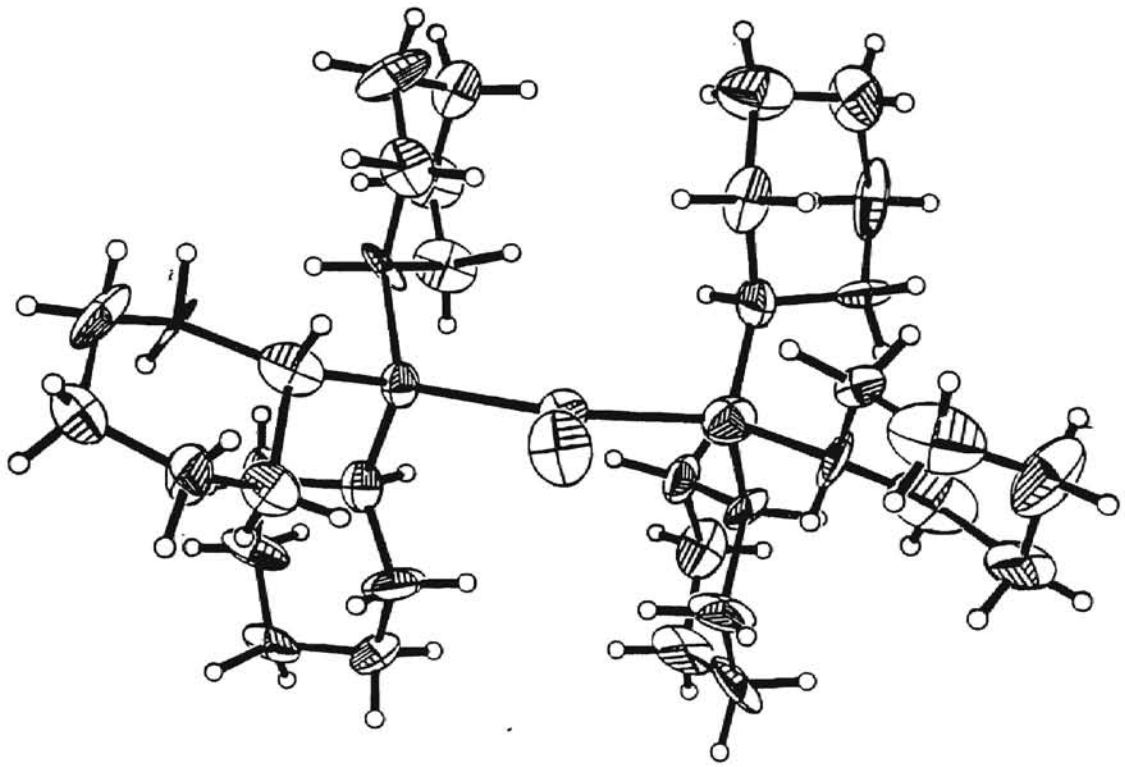


Figure 22. Projection view of [CuBr(P(C_6H_{11})3)2]

TABLE XLVI

CRYSTAL DATA FOR $CuBr(P(C_6H_{11})_3)_2$

Formula	$CuBrP_2C_{18}H_{30}$
MWT	263.4
a	18.084(2) Å
b	9.1150(10)
c	22.327(2)
α	90.0°
β	96.710(10)
γ	90.0
V	3655.1(7) $Å^3$
F (000)	1736
μMoK_a	3.462
λMoK_a	0.71073
D_{calc}	1.280 Mg m^{-3}
Z	8
Independent Refl.	4195
Obs. Refl. ($F<6.0\sigma(F)$)	1561
R/R_w	5.28/6.24%
Space Group	C2/c
Octants Meas.	$-1 \leq h \leq 23, -1 \leq k \leq 11,$ $-28 \leq l \leq 28$

TABLE XLVII

POSITIONAL PARAMETERS FOR
$CuBr(P(C_6H_{11})_3)_2$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Cu(1)	0000	3121(3)	2500
Br(1)	0000	5743(3)	2500
P(1)	0597(2)	2174(4)	3361(1)
C(11)	0053(7)	0898(15)	3784(5)
C(12)	-139(8)	-0562(18)	3443(6)
C(13)	-0564(9)	-1568(17)	3812(7)
C(14)	-1271(9)	-0854(18)	3965(7)
C(15)	-1113(8)	0594(19)	4299(6)
C(16)	-0661(8)	1614(16)	3933(7)
C(21)	1421(7)	1093(15)	3222(5)
C(22)	1902(8)	0426(16)	3759(5)
C(23)	2508(8)	-0567(18)	3564(6)
C(24)	2983(8)	0231(18)	3168(7)
C(25)	2534(10)	0919(19)	2635(7)
C(26)	1905(9)	1870(18)	2806(6)
C(31)	0862(8)	3644(16)	3918(6)
C(32)	1461(8)	4641(17)	3725(6)
C(33)	1545(10)	6029(18)	4114(7)
C(34)	1716(9)	5675(19)	4772(6)
C(35)	1155(9)	4600(21)	4970(6)
C(36)	1050(9)	3263(17)	4580(5)

TABLE XLVIII

HYDROGEN POSITIONAL PARAMETERS FOR
$CuBr(P(C_6H_{11})_3)_2$

ATOM	x	y	z
H(11A)	347	655	4157
H(12A)	310	-1031	3352
H(12B)	-438	-338	3070
H(13A)	-260	-1811	4180
H(13B)	-684	-2460	3593
H(14A)	-1539	-1502	4200
H(14B)	-1582	-634	3597
H(15A)	-818	367	4673
H(15B)	-1561	1067	4389
H(16A)	-962	1862	3564
H(16B)	-545	2503	4155
H(21A)	1226	265	2990
H(22A)	1590	-125	3996
H(22B)	2126	1214	4001
H(23A)	2279	-1379	3340
H(23B)	2813	-950	3910
H(24A)	3350	-413	3034
H(24B)	3237	1007	3398
H(25A)	2314	139	2386
H(25B)	2839	1492	2400
H(26A)	2130	2685	3031
H(26B)	1602	2252	2459
H(31A)	430	4258	3909
H(32A)	1336	4918	3311
H(32B)	1922	4111	3760
H(33A)	1091	6582	4053
H(33B)	1936	6631	3990
H(34A)	1729	6566	5002
H(34B)	2196	5219	4844
H(35A)	683	5096	4935
H(35B)	1284	4339	5386
H(36A)	1513	2736	4627
H(36B)	669	2635	4704

TABLE XLIX

ANISOTROPIC THERMAL PARAMETERS FOR
$CuBr(P(C_6H_{11})_3)_2$

ATOM	U11	U22	U33	U12	U13	U23
Cu(1)	60(2)	62(2)	58(2)	0	8(1)	0
Br(1)	111(2)	63(2)	108(2)	0	-11(2)	0
P(1)	63(3)	59(3)	54(2)	-8(2)	5(2)	3(2)
C(11)	44(8)	61(11)	68(8)	1(8)	-2(7)	7(8)
C(12)	77(10)	77(10)	83(9)	-15(11)	12(8)	0(11)
C(13)	96(13)	66(11)	102(12)	-25(11)	11(10)	-1(10)
C(14)	77(11)	92(15)	86(11)	-22(11)	16(9)	12(10)
C(15)	82(10)	94(12)	92(10)	-14(12)	7(9)	-13(12)
C(16)	72(11)	73(11)	99(11)	-19(10)	29(9)	0(10)
C(21)	75(9)	69(10)	51(7)	6(8)	-2(7)	-3(7)
C(22)	84(10)	72(11)	67(9)	-24(11)	20(8)	6(9)
C(23)	86(10)	68(9)	85(10)	-2(12)	5(9)	3(11)
C(24)	67(10)	84(13)	98(11)	-1(9)	13(9)	-20(10)
C(25)	116(14)	93(16)	92(12)	-4(12)	33(11)	-8(11)
C(26)	93(11)	82(11)	74(9)	8(12)	21(9)	29(10)
C(31)	81(11)	67(9)	62(9)	-15(9)	9(8)	6(8)
C(32)	90(10)	72(11)	69(9)	-13(10)	4(8)	2(9)
C(33)	134(15)	95(16)	96(13)	-40(12)	6(12)	12(11)
C(34)	117(13)	89(11)	91(12)	-36(14)	16(11)	-39(12)
C(35)	116(14)	118(15)	77(10)	-23(15)	22(10)	-2(12)
C(36)	114(13)	72(11)	62(9)	-23(11)	15(9)	-10(9)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE L

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $CuBr(P(C_6H_{11})_3)_2$

Cu(1)-Br(1)	2.390 (4)	Br(1)-Cu(1)-P(1)	112.4(1)
Cu(1)-P(1)	2.263 (3)	Br(1)-Cu(1)-P(1A)	112.4(1)
Cu(1)-P(1A)	2.263 (3)	P(1)-Cu(1)-P(1A)	135.1(2)
P(1)-C(11)	1.853 (14)	Cu(1)-P(1)-C(11)	116.3(4)
P(1)-C(21)	1.843 (14)	Cu(1)-P(1)-C(21)	112.1(4)
P(1)-C(31)	1.853 (14)	C(11)-P(1)-C(21)	103.8(6)
C(11)-C(12)	1.552 (20)	Cu(1)-P(1)-C(31)	110.8(5)
C(11)-C(16)	1.518 (19)	C(11)-P(1)-C(31)	102.9(6)
C(12)-C(13)	1.503 (22)	C(21)-P(1)-C(31)	110.4(6)
C(13)-C(14)	1.507 (23)	P(1)-C(11)-C(12)	112.9(9)
C(14)-C(15)	1.527 (23)	P(1)-C(11)-C(16)	111.0(10)
C(15)-C(16)	1.534 (22)	C(12)-C(11)-C(16)	109.2(10)
C(21)-C(22)	1.522 (17)	C(11)-C(12)-C(13)	110.7(11)
C(21)-C(26)	1.523 (20)	C(12)-C(13)-C(14)	111.2(13)
C(22)-C(23)	1.523 (21)	C(13)-C(14)-C(15)	111.6(13)
C(23)-C(24)	1.493 (22)	C(14)-C(15)-C(16)	110.1(12)
C(24)-C(25)	1.496 (21)	C(11)-C(16)-C(15)	112.1(12)
C(25)-C(26)	1.514 (24)	P(1)-C(21)-C(22)	118.7(9)
C(31)-C(32)	1.513 (21)	P(1)-C(21)-C(26)	112.8(10)
C(31)-C(36)	1.520 (18)	C(22)-C(21)-C(26)	110.5(11)
C(32)-C(33)	1.531 (22)	C(21)-C(22)-C(23)	112.1(11)
C(33)-C(34)	1.501 (21)	C(22)-C(23)-C(24)	111.3(13)
C(34)-C(35)	1.514 (25)	C(23)-C(24)-C(25)	112.3(12)
C(35)-C(36)	1.497 (23)	C(24)-C(25)-C(26)	113.2(13)
		C(21)-C(26)-C(25)	112.9(13)
		P(1)-C(31)-C(32)	112.4(10)
		P(1)-C(31)-C(36)	119.9(10)
		C(32)-C(31)-C(36)	109.2(11)
		C(31)-C(32)-C(33)	111.2(12)
		C(32)-C(33)-C(34)	111.9(13)
		C(33)-C(34)-C(35)	110.9(13)
		C(34)-C(35)-C(36)	113.6(13)
		C(31)-C(36)-C(35)	112.2(12)

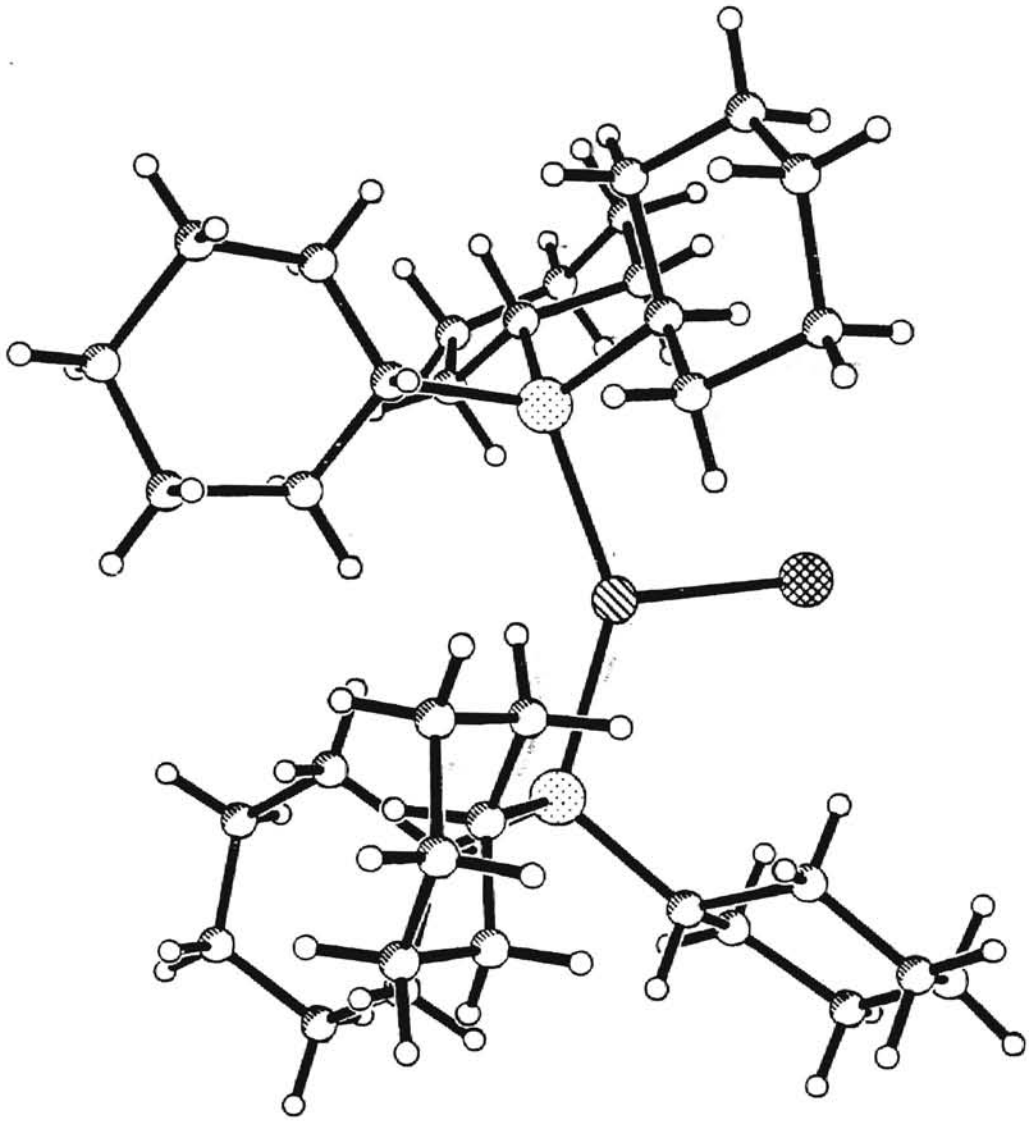


Figure 23. Projection view of $CuBr(P(C_6H_{11})_3)_2^*$

TABLE LI

CRYSTAL DATA FOR $CuBr(P(C_6H_{11})_3)_2$*

Formula	$CuBrP_2C_{36}H_{66}$
MWT	704.3
a	9.982(2) Å
b	15.571(3)
c	24.074(3)
α	90.0°
β	97.830(0)
γ	90.0
V	3707.0(9) $Å^3$
F (000)	1504
μMoK_a	1.776
λMoK_a	0.71073
D_{calc}	1.262 Mg m^{-3}
Z	4
Independent Refl.	8486
Obs. Refl. ($F<6.0\sigma(F)$)	1062
R/R_w	8.12/8.87%
Space Group	$P2_1/n$
Octants Meas.	$-1 \leq h \leq 12$, $-1 \leq k \leq 20$, $-31 \leq l \leq 31$

TABLE LII

POSITIONAL PARAMETERS FOR
$CuBr(P(C_6H_{11})_3)_2$*

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
Br(2)	3635(6)	878(3)	2225(2)
Cu(2)	4527(5)	2280(3)	2120(1)
P(1)	4708(10)	2936(6)	2977(3)
P(2)	4740(10)	2677(6)	1226(3)
C(111)	3078(32)	2894(24)	3246(12)
C(112)	3045(30)	3316(23)	3814(13)
C(113)	1654(54)	3190(25)	3972(13)
C(114)	467(39)	3557(24)	3550(16)
C(115)	562(33)	3218(20)	2953(14)
C(116)	2120(36)	3315(21)	2801(13)
C(121)	5883(37)	2397(20)	3511(11)
C(122)	7244(31)	2230(24)	3317(12)
C(123)	8126(37)	1635(26)	3702(14)
C(124)	7472(53)	892(24)	3963(13)
C(125)	6152(39)	1110(24)	4155(16)
C(126)	5236(30)	1567(21)	3720(12)
C(131)	5291(34)	4075(17)	3043(12)
C(132)	5975(39)	4356(24)	3602(15)
C(133)	6120(45)	5366(28)	3613(15)
C(134)	7172(46)	5550(22)	3160(16)
C(135)	6642(45)	5247(22)	2584(14)
C(136)	6222(39)	4270(19)	2617(12)
C(211)	3778(38)	2011(32)	692(12)
C(212)	4309(35)	1103(26)	630(13)
C(213)	3324(53)	557(26)	218(14)
C(214)	1914(49)	592(43)	301(19)
C(215)	1386(44)	1418(23)	309(16)
C(216)	2257(50)	1893(24)	750(16)
C(221)	4161(35)	3779(22)	1074(12)
C(222)	3668(38)	4041(23)	505(12)
C(223)	3487(42)	4977(25)	444(14)
C(224)	2430(45)	5349(20)	824(18)
C(225)	2927(46)	5084(30)	1405(17)
C(226)	3187(42)	4062(25)	1457(13)
C(231)	6580(29)	2618(26)	1060(12)
C(232)	6663(39)	2922(22)	424(10)
C(233)	8127(36)	2811(30)	310(14)
C(234)	9004(42)	3313(22)	715(17)
C(235)	9071(38)	3096(26)	1314(19)
C(236)	7548(46)	3134(26)	1479(12)

TABLE LIII

HYDROGEN POSITIONAL PARAMETERS FOR
$CuBr(P(C_6H_{11})_3)_2$*

ATOM	x	y	z
H(11A)	2841	2303	3288
H(11B)	3242	3916	3783
H(11C)	3706	3060	4092
H(11D)	1572	3433	4333
H(11E)	1461	2587	3985
H(11F)	695	4155	3530
H(11G)	-428	3519	3651
H(11H)	-72	3505	2679
H(11I)	306	2624	2964
H(11J)	2160	3030	2450
H(11K)	2342	3909	2758
H(12A)	6053	2740	3845
H(12B)	7664	2740	3198
H(12C)	7024	1868	2994
H(12D)	8403	2008	4014
H(12E)	8914	1478	3537
H(12F)	8082	625	4255
H(12G)	7301	492	3658
H(12H)	6290	1520	4455
H(12I)	5759	599	4288
H(12J)	5262	1204	3399
H(12K)	4317	1600	3795
H(13A)	4490	4417	2955
H(13B)	6799	4042	3703
H(13C)	5389	4245	3879
H(13D)	6599	5538	3969
H(13E)	5279	5674	3559
H(13F)	8052	5291	3229
H(13G)	7284	6162	3159
H(13H)	7165	5400	2292
H(13I)	5774	5519	2507
H(13J)	5821	4060	2257
H(13K)	7086	3997	2713
H(21A)	3802	2279	334
H(21B)	4227	823	979
H(21C)	5249	1104	582
H(21D)	3688	-13	208
H(21E)	3401	831	-133
H(21F)	1836	285	640
H(21G)	1413	284	-5

Table LIII (Continued)

H(21H)	466	1380	382
H(21I)	1395	1713	-41
H(21J)	1870	2452	783
H(21K)	2228	1594	1097
H(22A)	4964	4122	1153
H(22B)	2804	3767	414
H(22C)	4253	3839	248
H(22D)	3128	5125	66
H(22E)	4352	5250	533
H(22F)	1546	5111	718
H(22G)	2359	5964	807
H(22H)	2312	5270	1654
H(22I)	3779	5362	1517
H(22J)	3581	3922	1833
H(22K)	2330	3776	1381
H(23A)	6889	2034	1093
H(23B)	6370	3507	375
H(23C)	6076	2561	175
H(23D)	8221	2983	-66
H(23E)	8385	2218	353
H(23F)	8726	3902	675
H(23G)	9908	3275	623
H(23H)	9669	3457	1558
H(23I)	9363	2511	1368
H(23J)	7471	2948	1853
H(23K)	7280	3725	1442

TABLE LIV

ANISOTROPIC THERMAL PARAMETERS FOR
$CuBr(P(C_6H_{11})_3)_2$*

ATOM	U11	U22	U33	U12	U13	U23
Br(2)	254(7)	109(4)	108(3)	-80(4)	85(3)	-7(3)
Cu(2)	68(4)	81(3)	83(2)	-2(3)	40(2)	4(2)
P(1)	54(8)	81(7)	71(5)	1(6)	19(5)	2(5)
P(2)	64(8)	96(7)	62(5)	5(7)	16(5)	-5(5)
C(111)	50(27)	131(34)	70(20)	16(27)	16(20)	35(22)
C(112)	0(24)	184(39)	102(26)	-16(22)	71(20)	-40(22)
C(113)	225(67)	123(37)	68(22)	33(41)	13(35)	-30(21)
C(114)	81(41)	141(37)	141(32)	-25(31)	94(32)	8(30)
C(115)	40(29)	92(29)	131(28)	18(23)	41(22)	36(22)
C(116)	73(33)	90(27)	117(28)	-10(24)	95(26)	-34(22)
C(121)	90(34)	82(27)	56(17)	-9(26)	45(19)	-17(17)
C(122)	18(25)	143(34)	119(25)	17(27)	40(22)	47(25)
C(123)	73(36)	178(41)	116(27)	26(31)	63(26)	79(28)
C(124)	197(57)	104(34)	63(21)	32(40)	-24(29)	25(22)
C(125)	55(33)	61(28)	180(39)	30(25)	78(30)	24(24)
C(126)	0(24)	112(30)	116(25)	16(24)	46(21)	61(23)
C(131)	83(31)	32(18)7	5(19)	24(22)	1(24)	26(17)
C(132)	62(33)	94(38)	150(36)	-23(30)	48(29)	28(28)
C(133)	116(44)	130(45)	134(31)	-16(35)	47(32)	10(28)
C(134)	157(46)	70(30)	180(38)	-85(31)	74(41)	-8(26)
C(135)	175(51)	103(32)	99(26)	-16(33)	54(32)	73(23)
C(136)	142(39)	59(25)	95(23)	-19(28)	51(26)	27(19)
C(211)	7(27)	236(59)	72(21)	12(34)	15(20)	15(26)
C(212)	42(32)	135(36)	111(26)	58(29)	36(24)	-46(26)
C(213)	146(52)	111(35)	100(27)	1(37)	-10(35)	-64(24)
C(214)	26(42)	302(84)	130(37)	-9(51)	0(30)	-56(42)
C(215)	59(39)	63(28)	124(29)	-31(31)	21(28)	-16(24)
C(216)	117(46)	77(29)	135(35)	42(31)	82(32)	38(26)
C(221)	50(29)	126(36)	66(19)	51(25)	24(22)	44(20)
C(222)	111(38)	81(29)	103(25)	89(28)	56(24)	39(21)
C(223)	82(38)	106(36)	121(29)	29(32)	43(28)	12(24)
C(224)	131(50)	34(21)	164(36)	5(28)	13(40)	8(25)
C(225)	104(45)	185(54)	156(41)	69(40)	75(36)	-54(35)
C(226)	105(40)	121(35)	85(23)	97(33)	-5(26)	29(23)
C(231)	15(23)	166(39)	106(24)	27(27)	44(18)	0(25)
C(232)	100(39)	104(31)	68(20)	22(29)	36(21)	21(19)
C(233)	37(31)	188(47)	94(25)	44(33)	24(24)	-12(29)
C(234)	76(38)	78(30)	127(32)	39(27)	45(31)	5(25)
C(235)	10(29)	141(40)	186(45)	1(27)	55(28)	-35(30)
C(236)	140(48)	187(45)	48(17)	-28(36)	-37(27)	-38(21)

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE LV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
$CuBr(P(C_6H_{11})_3)_2$*

Br(2)-Cu(2)	2.384 (6)	Br(2)-Cu(2)-P(1)	107.3(3)
Cu(2)-P(1)	2.287 (8)	Br(2)-Cu(2)-P(2)	115.7(3)
Cu(2)-P(2)	2.276 (8)	P(1)-Cu(2)-P(2)	136.5(4)
P(1)-C(111)	1.833 (34)	Cu(2)-P(1)-C(111)	109.7(10)
P(1)-C(121)	1.821 (30)	Cu(2)-P(1)-C(121)	113.3(10)
P(1)-C(131)	1.867 (29)	C(111)-P(1)-C(121)	104.6(15)
P(2)-C(211)	1.821 (39)	Cu(2)-P(1)-C(131)	119.1(10)
P(2)-C(221)	1.833 (36)	C(111)-P(1)-C(131)	106.5(16)
P(2)-C(231)	1.935 (32)	C(121)-P(1)-C(131)	102.4(14)
C(111)-C(112)	1.520 (44)	Cu(2)-P(2)-C(211)	113.9(13)
C(111)-C(116)	1.487 (43)	Cu(2)-P(2)-C(221)	112.1(10)
C(112)-C(113)	1.502 (62)	C(211)-P(2)-C(221)	105.7(17)
C(113)-C(114)	1.561 (55)	Cu(2)-P(2)-C(231)	113.3(9)
C(114)-C(115)	1.546 (51)	C(211)-P(2)-C(231)	104.5(16)
C(115)-C(116)	1.652 (50)	C(221)-P(2)-C(231)	106.6(17)
C(121)-C(122)	1.518 (48)	P(1)-C(111)-C(112)	115.5(22)
C(121)-C(126)	1.559 (46)	P(1)-C(111)-C(116)	104.2(22)
C(122)-C(123)	1.507 (48)	C(112)-C(111)-C(116)	111.6(28)
C(123)-C(124)	1.507 (58)	C(111)-C(112)-C(113)	107.9(25)
C(124)-C(125)	1.494 (65)	C(112)-C(113)-C(114)	115.6(29)
C(125)-C(126)	1.477 (45)	C(113)-C(114)-C(115)	110.1(30)
C(131)-C(132)	1.488 (45)	C(114)-C(115)-C(116)	110.7(26)
C(131)-C(136)	1.507 (49)	C(111)-C(116)-C(115)	109.4(26)
C(132)-C(133)	1.580 (58)	P(1)-C(121)-C(122)	112.3(20)
C(133)-C(134)	1.640 (62)	P(1)-C(121)-C(126)	110.7(22)
C(134)-C(135)	1.491 (50)	C(122)-C(121)-C(126)	112.6(27)
C(135)-C(136)	1.583 (47)	C(121)-C(122)-C(123)	112.8(27)
C(211)-C(212)	1.525 (62)	C(122)-C(123)-C(124)	118.6(32)
C(211)-C(216)	1.554 (63)	C(123)-C(124)-C(125)	113.9(33)
C(212)-C(213)	1.551 (53)	C(124)-C(125)-C(126)	112.1(31)
C(213)-C(214)	1.448 (73)	C(121)-C(126)-C(125)	112.6(26)
C(214)-C(215)	1.391 (75)	P(1)-C(131)-C(132)	117.1(22)
C(215)-C(216)	1.476 (54)	P(1)-C(131)-C(136)	110.3(20)
C(221)-C(222)	1.449 (41)	C(132)-C(131)-C(136)	107.9(28)
C(221)-C(226)	1.494 (52)	C(131)-C(132)-C(133)	109.8(27)
C(222)-C(223)	1.474 (53)	C(132)-C(133)-C(134)	103.1(31)
C(223)-C(224)	1.597 (61)	C(133)-C(134)-C(135)	112.7(34)
C(224)-C(225)	1.477 (58)	C(134)-C(135)-C(136)	108.7(27)
C(225)-C(226)	1.614 (61)	C(131)-C(136)-C(135)	114.8(27)
C(231)-C(232)	1.617 (40)	P(2)-C(211)-C(212)	116.1(24)
C(231)-C(236)	1.526 (48)	P(2)-C(211)-C(216)	115.6(26)
C(232)-C(233)	1.533 (54)	C(212)-C(211)-C(216)	104.8(34)

Table LV (Continued)

C(233)-C(234)	1.448 (52)	C(211)-C(212)-C(213)	111.9(29)
C(234)-C(235)	1.472 (60)	C(212)-C(213)-C(214)	115.8(37)
C(235)-C(236)	1.624 (61)	C(213)-C(214)-C(215)	114.5(48)
		C(214)-C(215)-C(216)	106.6(35)
		C(211)-C(216)-C(215)	118.8(36)
		P(2)-C(221)-C(222)	120.6(24)
		P(2)-C(221)-C(226)	111.5(24)
		C(222)-C(221)-C(226)	109.6(29)
		C(221)-C(222)-C(223)	113.2(28)
		C(222)-C(223)-C(224)	112.5(31)
		C(223)-C(224)-C(225)	106.1(33)
		C(224)-C(225)-C(226)	112.3(32)
		C(221)-C(226)-C(225)	110.7(31)
		P(2)-C(231)-C(232)	110.8(21)
		P(2)-C(231)-C(236)	111.9(25)
		C(232)-C(231)-C(236)	111.2(29)
		C(231)-C(232)-C(233)	108.0(25)
		C(232)-C(233)-C(234)	108.9(32)
		C(233)-C(234)-C(235)	118.6(34)
		C(234)-C(235)-C(236)	108.2(30)
		C(231)-C(236)-C(235)	110.5(28)

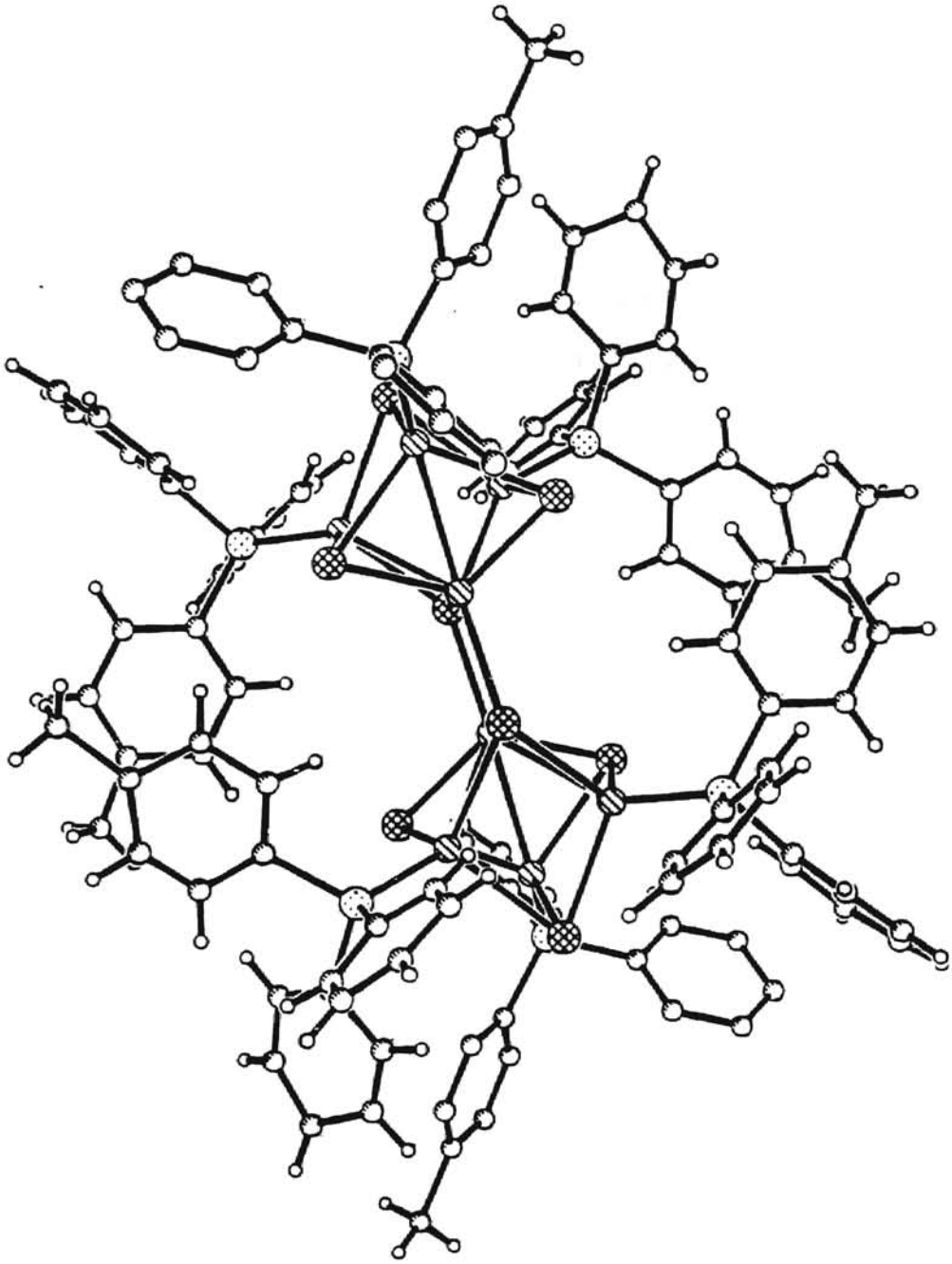


Figure 24. Projection view of $[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$

TABLE LVI

CRYSTAL DATA FOR $[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$

Formula	$CuIPC_{19}H_{17}$
MWT	467.74
a	12.319(2) Å
b	15.101(2)
c	16.511(3)
α	94.67°
β	105.75
γ	101.63
V	2865.2(8) $Å^3$
F (000)	1832
μMoK_a	3.783
λMoK_a	0.71073
D_{calc}	2.169 Mg m^{-3}
Z	8
Independent Refl.	10041
Obs. Refl. ($F>4.0\sigma(F)$)	2652
R/R_w	8.42/15.15%
Space Group	P_{-1}
Octants Meas.	$-1 \leq h \leq 14, -17 \leq k \leq 17,$ $-19 \leq l \leq 19$

TABLE LVII

POSITIONAL PARAMETERS FOR
$[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.1859	0.0071	0.0302
I2	0.3474(2)	0.1706(1)	0.2757(1)
I3	0.0505(2)	0.2409(1)	0.1102(1)
I4	0.003(6)	-0.0029(1)	0.2263(1)
Cu1	0.209(7)	0.005(5)	0.202(2)
Cu2	0.126(4)	0.174(8)	0.257(1)
Cu3	0.241(9)	0.182(9)	0.112(9)
Cu4	0.023(4)	0.063(5)	0.086(0)
P1	0.294(2)	-0.108(5)	0.248(5)
P2	0.092(5)	0.249(2)	0.360(0)
P3	0.355(3)	0.286(4)	0.064(7)
C10	0.424(2)	-0.112(2)	0.215(1)
C11	0.453(3)	-0.194(2)	0.192(2)
C12	0.558(3)	-0.188(3)	0.172(2)
C13	0.632(2)	-0.111(2)	0.171(2)
C14	0.601(3)	-0.032(2)	0.187(2)
C15	0.496(3)	-0.034(2)	0.211(2)
C110	0.342(2)	-0.103(2)	0.360(2)
C111	0.443(2)	-0.121(1)	0.404(1)
C112	0.472(2)	-0.125(2)	0.488(2)
C113	0.402(3)	-0.099(2)	0.534(2)
C114	0.298(3)	-0.075(2)	0.494(2)
C115	0.269(3)	-0.076(2)	0.405(2)
C120	0.204(2)	-0.225(2)	0.214(2)
C121	0.209(2)	-0.288(2)	0.269(2)
C122	0.134(2)	-0.377(2)	0.243(1)
C123	0.069(2)	-0.404(2)	0.159(2)
C124	0.066(2)	-0.341(2)	0.102(2)
C125	0.142(2)	-0.250(2)	0.129(2)
C126	-0.004(3)	-0.493(2)	0.121(2)
C20	0.123(3)	0.196(1)	0.464(1)
C21	0.236(2)	0.202(2)	0.513(2)
C22	0.258(2)	0.159(2)	0.585(2)
C23	0.166(4)	0.109(2)	0.608(1)
C24	0.052(3)	0.103(2)	0.559(2)
C25	0.031(2)	0.146(2)	0.487(2)
C210	-0.068(2)	0.260(2)	0.335(2)
C211	-0.155(3)	0.264(3)	0.263(2)
C212	-0.265(3)	0.268(2)	0.269(3)
C213	-0.286(3)	0.269(3)	0.347(3)
C214	-0.199(4)	0.265(5)	0.420(2)

Table LVII. (Continued)

C215	-0.089(3)	0.261(4)	0.414(2)
C220	0.175(2)	0.367(1)	0.402(2)
C221	0.155(2)	0.419(2)	0.467(2)
C222	0.225(3)	0.505(2)	0.501(1)
C223	0.316(2)	0.540(1)	0.470(2)
C224	0.337(2)	0.488(2)	0.404(2)
C225	0.266(2)	0.402(2)	0.370(1)
C226	0.410(3)	0.635(2)	0.502(2)
C24A	-0.258(6)	0.183(4)	0.300(4)
C21A	-0.080(7)	0.349(5)	0.312(5)
C25A	-0.153(6)	0.169(5)	0.321(4)
C22A	-0.176(7)	0.364(6)	0.318(5)
C30	0.397(2)	0.398(2)	0.129(2)
C31	0.339(3)	0.464(2)	0.117(2)
C32	0.371(3)	0.540(2)	0.178(2)
C33	0.469(3)	0.561(2)	0.251(2)
C34	0.519(3)	0.480(2)	0.262(2)
C35	0.492(3)	0.403(2)	0.206(2)
C310	0.287(3)	0.315(2)	-0.044(2)
C311	0.338(3)	0.392(2)	-0.069(2)
C312	0.293(3)	0.404(2)	-0.143(3)
C313	0.193(3)	0.353(2)	-0.203(2)
C314	0.144(2)	0.270(2)	-0.176(2)
C315	0.198(3)	0.253(2)	-0.092(2)
C316	0.138(4)	0.360(2)	-0.301(2)
C320	0.489(2)	0.260(2)	0.056(1)
C321	0.504(3)	0.171(2)	0.055(2)
C322	0.605(3)	0.151(2)	0.045(2)
C323	0.685(2)	0.223(2)	0.039(2)
C324	0.682(2)	0.311(2)	0.039(2)
C325	0.585(2)	0.327(2)	0.049(2)

TABLE LVIII

HYDROGEN POSITIONAL PARAMETERS FOR
$[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$

ATOM	x	y	z
H31A	0.274(3)	0.461(2)	0.068(2)
H32A	0.318(3)	0.580(2)	0.173(2)
H33A	0.498(3)	0.622(2)	0.282(2)
H34A	0.574(3)	0.484(2)	0.317(2)
H35A	0.537(3)	0.358(2)	0.218(2)
H31B	0.410(3)	0.431(2)	-0.034(2)
H31C	0.322(3)	0.462(2)	-0.159(3)
H31D	0.073(2)	0.230(2)	-0.211(2)
H31E	0.169(3)	0.199(2)	-0.070(2)
H31F	0.185(4)	0.415(2)	-0.309(2)
H31G	0.140(4)	0.310(2)	-0.340(2)
H31H	0.059(4)	0.366(2)	-0.311(2)
H32B	0.445(3)	0.123(2)	0.062(2)
H32C	0.612(3)	0.089(2)	0.039(2)
H32D	0.757(2)	0.212(3)	0.033(2)
H32E	0.743(3)	0.360(2)	0.035(2)
H32F	0.577(2)	0.389(2)	0.046(2)
H11A	0.403(3)	-0.251(2)	0.190(2)
H12A	0.581(3)	-0.243(3)	0.159(2)
H13A	0.704(3)	-0.112(2)	0.159(2)
H14A	0.642(3)	0.025(2)	0.177(2)
H15A	0.481(3)	0.019(2)	0.239(2)
H11B	0.499(2)	-0.133(1)	0.375(1)
H11C	0.543(3)	-0.138(2)	0.518(2)
H11D	0.418(3)	-0.109(2)	0.592(2)
H11E	0.252(3)	-0.054(2)	0.527(2)
H11F	0.198(3)	-0.061(2)	0.376(2)
H12B	0.263(2)	-0.272(2)	0.325(2)
H12C	0.122(2)	-0.418(2)	0.283(1)
H12D	0.021(2)	-0.355(2)	0.043(2)
H12E	0.148(2)	-0.206(2)	0.091(2)
H12F	-0.041(3)	-0.500(2)	0.060(2)
H12G	0.046(3)	-0.534(2)	0.132(2)
H12H	-0.062(3)	-0.507(2)	0.149(2)
H22F	0.480(3)	0.668(2)	0.493(2)
H22G	0.347(3)	0.661(2)	0.476(2)
H22H	0.420(3)	0.640(2)	0.562(2)

TABLE LIX

ANISOTROPIC THERMAL PARAMETERS FOR
$[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$

ATOM	U11	U22	U33	U12	U13	U23
I1	0.0424(1)	0.0422(10)	0.0500(11)	-0.0032(8)	0.0120(9)	0.0039(8)
I2	0.0430(1)	0.0503(11)	0.0603(12)	0.0027(9)	0.0095(10)	0.0086(9)
I4	0.0501(2)	0.0542(11)	0.0613(12)	0.0111(9)	0.0227(10)	0.0021(9)
I3	0.0455(1)	0.0478(10)	0.0563(12)	0.0094(9)	0.0147(9)	0.0142(9)
Cu3	0.049(2)	0.056(2)	0.078(2)	0.011(2)	0.027(2)	0.007(2)
Cu2	0.054(2)	0.074(2)	0.061(2)	-0.001(2)	0.018(2)	0.012(2)
Cu4	0.051(2)	0.065(2)	0.070(2)	0.007(2)	0.016(2)	0.003(2)
Cu1	0.052(2)	0.068(2)	0.076(3)	0.012(2)	0.019(2)	0.021(2)
P1	0.041(4)	0.047(4)	0.052(4)	-0.002(3)	0.009(4)	0.007(3)
P3	0.038(4)	0.047(4)	0.065(5)	-0.004(4)	0.021(4)	-0.003(3)
P2	0.046(5)	0.064(5)	0.041(4)	-0.003(4)	0.007(4)	0.013(4)
C30	0.045(17)	0.021(14)	0.092(23)	0.003(14)	0.046(17)	-0.008(13)
C31	0.148(35)	0.030(16)	0.097(26)	-0.023(17)	0.020(24)	0.011(20)
C32	0.124(33)	0.046(19)	0.179(39)	-0.032(22)	0.094(31)	0.022(21)
C33	0.079(27)	0.090(28)	0.134(35)	-0.002(25)	0.035(26)	-0.062(24)
C34	0.104(30)	0.091(26)	0.098(27)	-0.014(23)	0.042(23)	0.031(24)
C35	0.143(38)	0.063(23)	0.113(31)	0.000(22)	0.063(29)	-0.011(24)
C310	0.061(21)	0.043(17)	0.140(30)	0.007(19)	0.067(22)	0.015(16)
C311	0.075(24)	0.051(18)	0.080(24)	0.022(18)	0.013(21)	-0.039(17)
C312	0.071(28)	0.091(27)	0.129(34)	-0.007(27)	0.030(27)	0.007(22)
C313	0.073(23)	0.112(27)	0.033(17)	0.019(18)	0.012(17)	0.055(21)
C314	0.043(19)	0.032(16)	0.138(31)	-0.019(18)	-0.027(20)	0.005(14)
C315	0.084(25)	0.071(21)	0.052(20)	0.013(17)	0.017(19)	0.001(20)
C316	0.214(53)	0.190(43)	0.129(38)	-0.036(32)	0.026(37)	0.070(40)
C320	0.028(15)	0.072(19)	0.054(18)	0.008(15)	-0.013(13)	-0.022(15)
C321	0.087(25)	0.053(19)	0.115(27)	0.029(18)	0.057(22)	0.021(18)
C322	0.093(26)	0.069(22)	0.132(29)	0.026(20)	0.067(24)	0.073(21)
C323	0.026(17)	0.123(28)	0.066(21)	0.018(22)	0.015(15)	0.028(20)
C324	0.045(20)	0.086(23)	0.112(27)	-0.017(21)	0.049(19)	-0.051(19)
C325	0.039(17)	0.044(16)	0.141(28)	0.018(17)	0.058(19)	-0.017(14)
C10	0.071(21)	0.069(19)	0.030(15)	-0.002(14)	0.014(14)	0.033(17)
C11	0.127(34)	0.042(19)	0.107(28)	0.012(18)	0.022(25)	0.014(21)
C12	0.077(28)	0.162(40)	0.066(23)	-0.023(24)	0.031(22)	0.061(27)
C13	0.051(22)	0.104(27)	0.080(23)	-0.007(21)	0.025(19)	0.037(21)
C14	0.114(32)	0.095(27)	0.138(33)	0.034(23)	0.059(27)	0.056(24)
C15	0.103(27)	0.052(20)	0.124(28)	0.031(18)	0.075(23)	0.047(20)
C120	0.036(17)	0.077(20)	0.120(27)	0.068(21)	0.033(18)	0.048(16)
C121	0.055(20)	0.067(20)	0.075(22)	-0.025(17)	-0.011(17)	0.013(17)
C122	0.066(20)	0.101(23)	0.015(14)	0.008(14)	0.001(14)	0.010(18)
C123	0.049(18)	0.055(18)	0.062(20)	-0.025(16)	-0.002(16)	0.014(15)
C124	0.070(22)	0.078(21)	0.033(17)	-0.007(16)	-0.026(16)	0.016(18)
C125	0.051(19)	0.119(26)	0.024(15)	0.011(16)	0.012(14)	0.033(19)
C126	0.154(36)	0.083(24)	0.087(25)	-0.012(20)	0.028(25)	-0.020(25)

TABLE LIX (Continued)

C226	0.181(44)	0.057(23)	0.262(51)	0.026(28)	-0.031(39)	-0.079(27)

The anisotropic displacement exponent takes the form:

$$\exp(-2\pi(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$$

x 10^3 for I, Cu and P, x 10^2 for C.

TABLE LX

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR $[Cu_4I_4(P(Ph_2(p\text{-toly})))_3]_2$

I1 Cu1	2.780(3)	Cu4 I1 Cu4	71.11(11)
I1 Cu3	2.734(3)	Cu4 I1 Cu3	62.73(9)
I1 Cu4	2.666(3)	Cu4 I1 Cu3	120.79(10)
I1 Cu4	2.707(3)	Cu4 I1 Cu1	64.09(10)
I2 Cu1	2.707(4)	Cu4 I1 Cu1	119.65(10)
I2 Cu2	2.666(4)	Cu3 I1 Cu1	70.10(9)
I2 Cu3	2.688(4)	Cu2 I2 Cu3	70.17(10)
I3 Cu2	2.709(4)	Cu2 I2 Cu1	70.20(11)
I3 Cu3	2.662(4)	Cu3 I2 Cu1	71.90(10)
I3 Cu4	2.630(4)	Cu4 I4 Cu1	66.09(11)
I4 Cu1	2.657(4)	Cu4 I4 Cu2	67.22(10)
I4 Cu2	2.724(4)	Cu1 I4 Cu2	70.08(11)
I4 Cu4	2.645(4)	Cu4 I3 Cu3	64.17(10)
Cu3 P3	2.252(7)	Cu4 I3 Cu2	67.65(10)
Cu3 Cu4	2.811(4)	Cu3 I3 Cu2	69.91(11)
Cu2 P2	2.249(7)	P3 Cu3 I3	107.5(2)
Cu2 Cu4	2.973(5)	P3 Cu3 I2	110.0(2)
Cu4 I1	2.707(3)	I3 Cu3 I2	107.39(12)
Cu4 Cu1	2.891(5)	P3 Cu3 I1	115.7(2)
Cu1 P1	2.243(7)	I3 Cu3 I1	111.05(11)
P1 C110	1.78(2)	I2 Cu3 I1	104.94(11)
P1 C10	1.83(3)	P3 Cu3 Cu4	148.2(2)
P1 C120	1.84(3)	I3 Cu3 Cu4	57.37(10)
P3 C320	1.82(3)	I2 Cu3 Cu4	101.59(13)
P3 C30	1.82(2)	I1 Cu3 Cu4	57.44(9)
P3 C310	1.87(3)	P2 Cu2 I2	116.0(2)
P2 C20	1.84(2)	P2 Cu2 I3	112.1(2)
P2 C210	1.93(2)	I2 Cu2 I3	106.64(12)
P2 C220	1.82(2)	P2 Cu2 I4	109.6(2)
C30 C31	1.34(3)	I2 Cu2 I4	107.32(13)
C30 C35	1.45(4)	I3 Cu2 I4	104.54(11)
C31 C32	1.38(3)	P2 Cu2 Cu4	146.0(2)
C32 C33	1.41(4)	I2 Cu2 Cu4	98.03(12)
C33 C34	1.49(4)	I3 Cu2 Cu4	54.91(9)
C34 C35	1.35(3)	I4 Cu2 Cu4	55.12(9)
C310 C315	1.30(3)	I3 Cu4 I4	109.08(13)
C310 C311	1.36(3)	I3 Cu4 I1	114.28(12)
C311 C312	1.24(4)	I4 Cu4 I1	112.55(13)
C312 C313	1.38(4)	I3 Cu4 I1	107.00(12)
C313 C314	1.44(4)	I4 Cu4 I1	104.42(11)
C313 C316	1.59(4)	I1 Cu4 I1	108.89(11)
C314 C315	1.43(3)	I3 Cu4 Cu3	58.46(10)
C320 C321	1.37(3)	I4 Cu4 Cu3	111.85(14)
C320 C325	1.45(3)	I1 Cu4 Cu3	59.83(9)

Table LX. (Continued)

C321 C322	1.37(3)	I1 Cu4 Cu3	143.60(15)
C322 C323	1.35(4)	I3 Cu4 Cu1	111.79(13)
C323 C324	1.33(3)	I4 Cu4 Cu1	57.15(10)
C324 C325	1.32(3)	I1 Cu4 Cu1	59.88(10)
C10 C15	1.35(3)	I1 Cu4 Cu1	140.73(14)
C10 C11	1.40(3)	I3 Cu4 Cu2	57.44(10)
C11 C12	1.39(4)	I4 Cu4 Cu2	57.65(10)
C12 C13	1.33(4)	I1 Cu4 Cu2	110.92(13)
C13 C14	1.35(3)	I1 Cu4 Cu2	140.14(14)
C14 C15	1.45(4)	Cu3 Cu4 Cu1	67.46(12)
C110 C111	1.38(3)	Cu3 Cu4 Cu2	64.21(11)
C110 C115	1.41(3)	Cu1 Cu4 Cu2	63.58(11)
C111 C112	1.34(3)	P1 Cu1 I4	115.5(2)
C112 C113	1.37(3)	P1 Cu1 I2	110.9(2)
C113 C114	1.41(4)	I4 Cu1 I2	108.07(12)
C114 C115	1.41(3)	P1 Cu1 I1	109.8(2)
C120 C121	1.36(3)	I4 Cu1 I1	108.63(12)
C120 C125	1.37(3)	I2 Cu1 I1	103.17(11)
C121 C122	1.43(3)	P1 Cu1 Cu4	149.6(2)
C122 C123	1.38(3)	I4 Cu1 Cu4	56.76(10)
C123 C124	1.40(3)	I2 Cu1 Cu4	99.08(12)
C123 C126	1.45(3)	I1 Cu1 Cu4	56.03(9)
C124 C125	1.45(3)	C110 P1 C10	103.7(11)
C20 C21	1.39	C110 P1 C120	101.6(12)
C20 C25	1.39	C10 P1 C120	103.7(12)
C21 C22	1.39	C110 P1 Cu1	114.9(8)
C22 C23	1.39	C10 P1 Cu1	115.0(9)
C23 C24	1.39	C120 P1 Cu1	116.1(8)
C24 C25	1.39	C320 P3 C30	106.3(12)
C210 C211	1.39	C320 P3 C310	104.2(11)
C210 C215	1.39	C30 P3 C310	101.7(13)
C210 C21A	1.46(8)	C320 P3 Cu3	115.6(9)
C210 C25A	1.51(7)	C30 P3 Cu3	111.7(8)
C211 C212	1.39	C310 P3 Cu3	115.9(9)
C211 C21A	1.46(8)	C220 P2 C20	103.9(11)
C211 C25A	1.79(7)	C220 P2 C210	103.7(12)
C211 C24A	1.84(7)	C20 P2 C210	109.9(15)
C211 C22A	1.79(9)	C220 P2 Cu2	115.8(10)
C212 C213	1.39	C20 P2 Cu2	113.2(7)
C212 C24A	1.43(7)	C210 P2 Cu2	109.7(11)
C212 C22A	1.62(8)	C31 C30 C35	122.1(27)
C213 C214	1.39	C31 C30 P3	125.4(24)
C213 C24A	1.60(7)	C35 C30 P3	112.0(22)
C213 C22A	1.96(9)	C30 C31 C32	118.8(32)
C214 C215	1.39	C31 C32 C33	126.3(35)
C215 C25A	1.85(8)	C32 C33 C34	109.4(31)
C220 C221	1.39	C35 C34 C33	126.6(37)

Table LX. (Continued)

C220 C225	1.39	C34 C35 C30	115.7(35)
C221 C222	1.39	C315 C310 C311	124.7(33)
C222 C223	1.39	C315 C310 P3	115.7(22)
C223 C224	1.39	C311 C310 P3	119.4(26)
C223 C226	1.60(3)	C312 C311 C310	115.9(33)
C224 C225	1.39	C311 C312 C313	130.0(37)
C24A C25A	1.31(9)	C312 C313 C314	112.7(27)
C21A C22A	1.27(11)	C312 C313 C316	131.9(35)
		C314 C313 C316	114.3(31)
		C315 C314 C313	118.3(24)
		C310 C315 C314	118.1(28)
		C321 C320 C325	116.1(26)
		C321 C320 P3	121.8(20)
		C325 C320 P3	122.1(21)
		C320 C321 C322	120.6(28)
		C323 C322 C321	115.8(26)
		C324 C323 C322	129.6(27)
		C325 C324 C323	113.2(25)
		C324 C325 C320	124.6(27)
		C15 C10 C11	116.4(27)
		C15 C10 P1	119.2(21)
		C11 C10 P1	124.3(26)
		C12 C11 C10	118.6(30)
		C13 C12 C11	125.7(34)
		C12 C13 C14	116.9(32)
		C13 C14 C15	119.7(32)
		C10 C15 C14	122.5(27)
		C111 C110 C115	119.2(23)
		C111 C110 P1	124.4(20)
		C115 C110 P1	116.3(20)
		C112 C111 C110	121.3(25)
		C111 C112 C113	120.3(29)
		C112 C113 C114	121.7(31)
		C115 C114 C113	117.0(33)
		C110 C115 C114	119.9(29)
		C121 C120 C125	121.0(28)
		C121 C120 P1	120.6(24)
		C125 C120 P1	118.0(21)
		C120 C121 C122	119.7(26)
		C123 C122 C121	119.8(25)
		C122 C123 C124	119.9(24)
		C122 C123 C126	127.4(29)
		C124 C123 C126	112.6(25)
		C123 C124 C125	118.8(22)
		C120 C125 C124	119.4(25)
		C21 C20 C25	120.0
		C21 C20 P2	121.1(20)

Table LX. (Continued)

C25 C20 P2	118.9(20)
C20 C21 C22	120.0
C23 C22 C21	120.0
C22 C23 C24	120.0
C23 C24 C25	120.0
C24 C25 C20	120.0
C211 C210 C215	120.0
C211 C210 C21A	61.6(35)
C215 C210 C21A	104.0(38)
C211 C210 C25A	76.2(31)
C215 C210 C25A	79.2(33)
C21A C210 C25A	133.0(48)
C211 C210 P2	139.5(23)
C215 C210 P2	100.5(23)
C21A C210 P2	112.6(37)
C25A C210 P2	112.7(32)
C210 C211 C212	120.0
C210 C211 C21A	61.5(33)
C212 C211 C21A	104.1(37)
C210 C211 C25A	55.0(24)
C212 C211 C25A	91.6(26)
C21A C211 C25A	113.4(41)
C210 C211 C24A	89.3(23)
C212 C211 C24A	50.2(22)
C21A C211 C24A	125.5(42)
C25A C211 C24A	42.4(29)
C210 C211 C22A	88.4(30)
C212 C211 C22A	59.6(29)
C21A C211 C22A	44.5(39)
C25A C211 C22A	114.4(38)
C24A C211 C22A	94.7(37)
C213 C212 C211	120.0
C213 C212 C24A	69.2(32)
C211 C212 C24A	81.4(30)
C213 C212 C22A	80.7(35)
C211 C212 C22A	72.6(34)
C24A C212 C22A	122.3(45)
C212 C213 C214	120.0
C212 C213 C24A	56.5(26)
C214 C213 C24A	89.1(27)
C212 C213 C22A	54.8(27)
C214 C213 C22A	88.5(28)
C24A C213 C22A	96.8(37)
C215 C214 C213	120.0
C214 C215 C210	120.0
C214 C215 C25A	91.5(26)
C210 C215 C25A	53.3(25)

Table LX. (Continued)

C221 C220 C225	120.0
C221 C220 P2	118.8(20)
C225 C220 P2	120.8(19)
C222 C221 C220	120.0
C221 C222 C223	120.0
C222 C223 C224	120.0
C222 C223 C226	127.7(28)
C224 C223 C226	112.2(28)
C223 C224 C225	120.0
C224 C225 C220	120.0
C25A C24A C212	113.9(57)
C25A C24A C213	120.4(57)
C212 C24A C213	54.3(23)
C25A C24A C211	67.0(43)
C212 C24A C211	48.4(21)
C213 C24A C211	88.6(30)
C22A C21A C210	110.0(72)
C22A C21A C211	81.8(63)
C210 C21A C211	57.0(29)
C24A C25A C210	108.0(56)
C24A C25A C211	70.6(45)
C210 C25A C211	48.9(21)
C24A C25A C215	97.2(52)
C210 C25A C215	47.5(21)
C211 C25A C215	82.7(28)
C21A C22A C212	101.3(67)
C21A C22A C211	53.6(51)
C212 C22A C211	47.8(23)
C21A C22A C213	120.4(69)
C212 C22A C213	44.5(22)
C211 C22A C213	79.8(32)

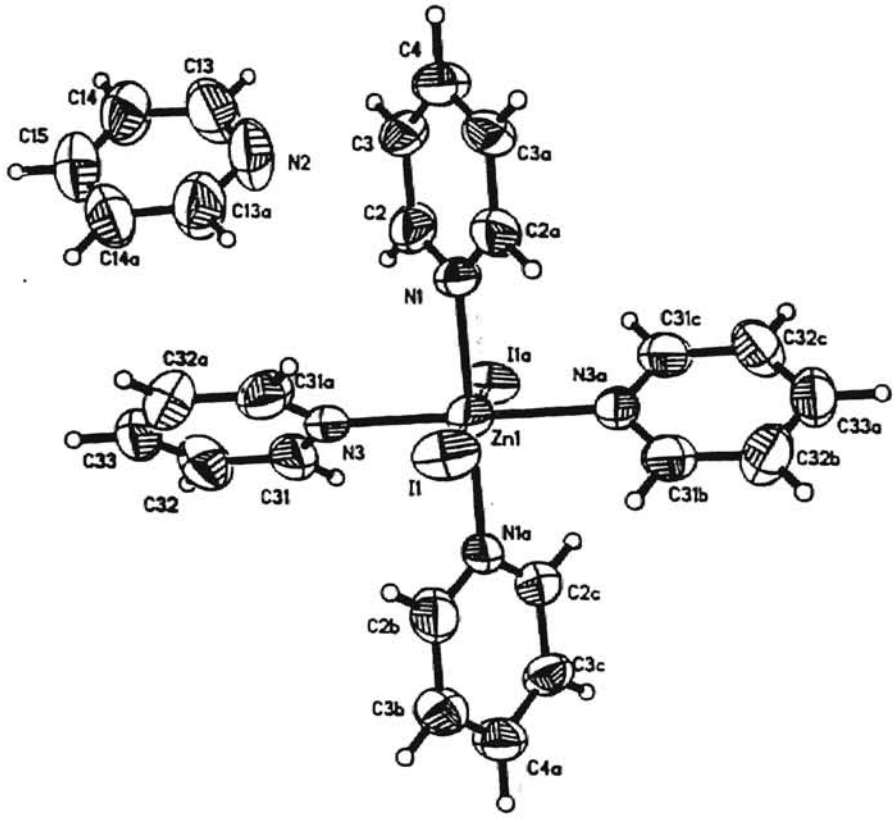


Figure 25. Projection view of $Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$

TABLE LXI

CRYSTAL DATA FOR $Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$

Formula	$ZnI_2NC_{30}H_{30}$
MWT	792.11
a	12.313(1) Å
b	15.335(2)
c	16.616(2)
α	90.0°
β	90.0
γ	90.0
V	3137.4(7) $Å^3$
F (000)	1552
μMoK_a	35.40 cm^{-1}
λMoK_a	0.71073 Å
D_{calc}	1.676 Mg m^{-3}
Z	4
Independent Refl.	1348
Obs. Refl. ($F>4.0\sigma(F)$)	493
R/R_w	3.6/4.4%
Space Group	Ccca
Octants Meas.	$-1 \leq h \leq 13, -1 \leq k \leq 16$
	$-1 \leq l \leq 17$

TABLE LXII

POSITIONAL PARAMETERS FOR
$Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$

ATOM	x (SIG (x))	y (SIG (y))	z (SIG (z))
I1	0.7810 (1)	0.7500	0.2500
Cu1	0.5000	0.7500	0.2500
Zn1	0.5000	0.7500	0.2500
N1	0.5000	0.6185 (7)	0.2500
N2	0.2500	0.5000	0.0499 (10)
N3	0.5000	0.7500	0.1261 (7)
C1	0.4227 (11)	0.4871 (7)	0.2086 (7)
C2	0.4246 (12)	0.5736 (9)	0.2101 (7)
C4	0.5000	0.4382 (9)	0.2500
C13	0.1789 (14)	0.4557 (12)	0.0071 (8)
C14	0.1747 (13)	0.4519 (11)	-00747 (9)
C15	0.2500	0.5000	-0.1129 (14)
C31	0.4229 (13)	0.7893 (8)	0.0844 (8)
C32	0.4184 (14)	0.7902 (10)	0.0018 (10)
C33	0.5000	0.7500	-0.0401 (11)

TABLE LXIII

HYDROGEN POSITIONAL PARAMETERS FOR
$Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$

ATOM	x	y	z
H3A	3663	4540	1797
H2A	3724	6064	1798
H4A	5000	3757	2500
H13A	1240	4234	371
H14A	1233	4165	-1035
H15A	2500	5000	-1707
H31A	3675	8196	1136
H32A	3582	8182	-240
H33A	5000	7500	-981

TABLE LXIV

ANISOTROPIC THERMAL PARAMETERS FOR
$Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$

ATOM	U11	U22	U33	U12	U13	U23
I1	56 (1)	43 (1)	83 (1)	0	0	-5 (2)
Zn1	313 (7)	35 (2)	44(2)	0	0	0
C3	57 (10)	42 (10)	56 (8)	10 (8)	9 (8)	-7 (7)
C2	97 (13)	52 (9)	47 (9)	24 (9)	-7 (9)	-4 (7)
C4	63 (12)	38 (9)	65 (11)	0	-9 (22)	0
N3	138 (15)	31 (7)	41 (8)	-17 (20)	0	0
C33	110 (18)	67 (13)	42 (11)	-26 (27)	0	0
N2	103 (22)	134 (20)	46 (15)	-29 (16)	0	0
C15	88 (23)	120 (22)	49 (16)	11 (17)	0	0
C13	127 (18)	114 (14)	63 (13)	-41 (15)	-4 (12)	13 (12)
C14	110 (16)	103 (14)	58 (12)	-12 (13)	-15 (11)	-12 (10)
C31	104 (14)	44 (8)	61 (13)	11 (9)	25 (9)	5 (8)
C32	101 (14)	73 (10)	58 (11)	-3 (13)	-8 (9)	18 (9)
N1	129 (14)	31 (7)	40 (8)	0	-21 (19)	0

The anisotropic displacement exponent takes the form:

$$-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$$

TABLE LXV

BOND DISTANCES (Å) AND BOND ANGLES (°) FOR
$Cu_{0.92}Zn_{0.08}I_2(C_5H_5N)_4 \cdot C_5H_5N$

Zn1-N1	2.014 (13)	N3 - Zn1 - N1	90.0 (1)
Zn1-N3	2.062 (13)	C2 - C3 - C4	119.0 (13)
N1-C2	1.323 (17)	C15 - C14 - C13	115.4 (18)
N3-C31	1.330 (18)	C33 - C32 - C31	118.8 (17)
N2-C13	1.323 (21)	C3 - C2 - N1	122.8 (14)
C2-C3	1.383 (19)	Zn1 - N3 - C31	121.8 (8)
C3-C4	1.370 (16)	N2 - C13 - C14	125.2 (17)
C13-C14	1.361 (21)	N3 - C31 - C32	124.2 (15)
C14-C15	1.356 (21)	Zn1 - N1 - C2	121.0 (8)
C31-C32	1.341 (24)	N1 - Zn1 - N3A	90.0 (1)
C32-C33	1.387 (21)	N1 - Zn1 - N1A	180.0 (1)
Zn1-N3A	2.062 (13)	C3 - C4 - C3A	118.4 (15)
N1-C2A	1.323 (17)	Zn1-N3-C31A	121.8 (8)
Zn1-N1A	2.014 (13)	C32-C33-C32A	117.5 (21)
C3A-C4	1.370 (16)	C13-C15-C14A	123.1 (23)
N3-C31A	1.330 (18)	Zn1-N1-C2A	121.0 (8)
C32A-C33	1.387 (21)	N3-Zn1-N3A	180.0 (1)
N2-C13A	1.323 (21)	N3 - Zn1 - N1A	90.0 (1)
C14A-C15	1.356 (21)	N3A - Zn1 - N1A	90.0 (1)
		C31 - N3 - C31A	116.3 (17)
		C13 - N2 - C13A	115.6 (19)
		C2 - N1 - C2A	118.0 (16)

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